

Article

First-Principles Study of Doped CdX ($X = Te, Se$) Compounds: Enhancing Thermoelectric Properties

Junfeng Jin ¹, Fang Lv ², Wei Cao ^{1,2,*}  and Ziyu Wang ^{1,2,*}
¹ The Institute of Technological Sciences, Wuhan University, Wuhan 430060, China; 2021206520035@whu.edu.cn

² Key Laboratory of Artificial Micro- and Nano- Structures of Ministry of Education, School of Physics and Technology, Wuhan University, Wuhan 430072, China; fanglv@whu.edu.cn

* Correspondence: wei_cao@whu.edu.cn (W.C.); zywang@whu.edu.cn (Z.W.)

Abstract: Isovalent doping offers a method to enhance the thermoelectric properties of semiconductors, yet its influence on the phonon structure and propagation is often overlooked. Here, we take CdX ($X = Te, Se$) compounds as an example to study the role of isovalent doping in thermoelectrics by first-principles calculations in combination with the Boltzmann transport theory. The electronic and phononic properties of Cd_8Se_8 , Cd_8Se_7Te , Cd_8Te_8 , and Cd_8Te_7Se are compared. The results suggest that isovalent doping with CdX significantly improves the thermoelectric performance. Due to the similar properties of Se and Te atoms, the electronic properties remain unaffected. Moreover, doping enhances anharmonic phonon scattering, leading to a reduction in lattice thermal conductivity. Our results show that optimized p-type(n-type) ZT values can reach 3.13 (1.33) and 2.51 (1.21) for Cd_8Te_7Se and Cd_8Se_7Te at 900 K, respectively. This research illuminates the potential benefits of strategically employing isovalent doping to enhance the thermoelectric properties of CdX compounds.

Keywords: thermoelectric; doped CdX compounds; first-principles calculations; isovalent doping



Citation: Jin, J.; Lv, F.; Cao, W.; Wang, Z. First-Principles Study of Doped CdX ($X = Te, Se$) Compounds: Enhancing Thermoelectric Properties. *Materials* **2024**, *17*, 1797. <https://doi.org/10.3390/ma17081797>

Academic Editor: Yaniv Gelbstein

Received: 18 March 2024

Revised: 4 April 2024

Accepted: 4 April 2024

Published: 14 April 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

One of the primary byproducts of using various energy forms is heat. The process of converting this excess heat into electrical energy, known as thermoelectricity, is seen as a promising technology for practical energy harvesting applications [1]. The efficiency of thermoelectric conversion is assessed using the dimensionless thermoelectric figure of merit ZT [2]. ZT is defined as

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_l} \quad (1)$$

where σ , S , T , κ_e and κ_l represent electrical conductivity, Seebeck coefficient, temperature, electronic thermal conductivity, and lattice thermal conductivity, respectively. However, the coupling effects in thermoelectric performance make it challenging to directly enhance the thermoelectric properties [3]. This is due to the intricate interplay between electrical conductivity, thermal conductivity, and Seebeck coefficient, which are often coupled together. Improving one of these properties can inadvertently affect the others, making it difficult to achieve substantial enhancements in overall thermoelectric performance without carefully considering and addressing these interdependent factors. Consequently, targeted strategies that can effectively decouple these properties or optimize their collective interaction are crucial for achieving significant advancements in thermoelectric materials. Various strategies, including doping [4], band engineering [5], phonon engineering [6], nanostructuring [7], and alloying [8], have been proposed to enhance thermoelectric performance.

Doping in thermoelectric materials enables precise tuning of electronic properties, providing flexibility, versatility, and compatibility with other enhancement techniques. There are many types of doping in thermoelectric materials, including cationic doping [9],

co-doping [10], ion doping [11] and single-atom doping [12]. Here, we primarily focus on single-atom doping. Based on the doping atoms, doping in thermoelectric materials can be classified into aliovalent doping, which involves introducing impurities of different valences, and isovalent doping, which involves introducing impurities of the same valence. Aliovalent doping is commonly utilized to regulate carrier concentration for optimizing ZT . Research on the effects of Nb doping on the thermoelectric properties of n-type half-Heusler compounds revealed an enhanced power factor and a 20% increase attributed to aliovalent doping-induced decoupling between thermoelectric parameters [13]. Han et al. [14] emphasized the critical impact of aliovalent dopants on controlling the phonon structure and inhibiting the phonon propagation in a heavy-band $NbFeSb$ system. Baranets et al. [15] demonstrated that aliovalent substitutions can alter the dimensionality of the polyanionic sublattice in the resulting quaternary phases, leading to reduced electrical resistivity and a notably enhanced Seebeck coefficient.

Compared to aliovalent doping, isovalent doping ideally decouples and regulates thermoelectric performance by reducing thermal conductivity through phonon scattering while maintaining unchanged electronic properties. Musah et al. [16] summarized a review of isovalent substitution as a method to independently enhance thermoelectric performance and device applications. The substitution of isovalent ions in the anion Te -site of $Bi-Sb-Te$ led to a significant enhancement of the ZT over a wide temperature range, with the ZT being increased by 10% for all measured temperatures and averaging beyond 1.0 between 300 and 520 K, demonstrating the synergetic control of band structure and deformation potential via isovalent substitution [17]. He et al. [18] also demonstrated that isovalent Te substitution effectively reduces κ_l and increases σ in hole carrier concentration.

To thoroughly explore the impact of equiatomic doping on regulating thermoelectric performance, we chose CdX ($X = Se, Te$) as the focus of our research and utilized a first-principles approach. Recent research [19,20] indicated that CdX is commonly used as a dopant in thermoelectric applications. The simple cubic phase structure of CdX provides advantages for first-principles studies due to its well-defined symmetry and straightforward electronic and phononic property calculations. Additionally, Te and Se share similarities in their doping characteristics, owing to their comparable chemical properties and the analogous effects they induce when integrated into host materials. In this paper, we systematically investigated the electronic, phononic, mechanical, bonding, and thermoelectric properties of CdX using first-principles combined with Boltzmann transport theory.

2. Computational Methods

Theoretical computations were conducted using density functional theory (DFT) within the Quantum ESPRESSO v6.2 (QE) code [21,22]. The exchange–correlation functional used is the Generalized Gradient Approximation (GGA) as given by Perdew–Burke–Ernzerhof (PBE) [23], and the corresponding pseudopotential files are sourced from the standard solid-state pseudopotentials (SSSP PBE Efficiency v1.3.0) library [24]. A kinetic energy cut-off of 80 Ry was utilized, and all relaxations were carried out until the forces and energy on each atom were reduced to less than 10^{-4} Ry/Bohr and 10^{-10} Ry. The Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional [25,26] was used to obtain a more accurate band structure for the primitive cell of CdX . We constructed the doping structure using a $2 \times 2 \times 2$ supercell of the primitive cell for both $CdTe$ and $CdSe$. The Brillouin zone was sampled over a uniform Γ -centered k -mesh of $4 \times 4 \times 4$. The projected crystal orbital Hamilton population (COHP) was calculated using the LOBSTER [27,28] package. The mechanical properties were carried out using Voigt–Reuss–Hill approximation [29], as implemented in the ElATools v1.7.0 [30] package. The crystal structure was plotted using VESTA v3.5.7 software [31].

Boltzmann’s transport theory was employed to analyze the transport properties of systems using the BoltzTraP code [32]. Under Boltzmann’s transport theory, these electronic transport coefficients can be expressed as

$$S_{\alpha\beta}(T, \mu) = \frac{1}{eT} \frac{\int v_{\alpha}(i, \mathbf{k}) v_{\beta}(i, \mathbf{k}) (\varepsilon - \mu) \left[-\frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon}{\int v_{\alpha}(i, \mathbf{k}) v_{\beta}(i, \mathbf{k}) \left[-\frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon} \quad (2)$$

$$\frac{\sigma_{\alpha\beta}(T, \mu)}{\tau_e(i, \mathbf{k})} = \frac{1}{V} \int e^2 v_{\alpha}(i, \mathbf{k}) v_{\beta}(i, \mathbf{k}) \left[-\frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (3)$$

$$\frac{\kappa_{\alpha\beta}^e(T, \mu)}{\tau(i, \mathbf{k})} = \frac{1}{TV} \int v_{\alpha}(i, \mathbf{k}) v_{\beta}(i, \mathbf{k}) (\varepsilon - \mu)^2 \left[-\frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon \quad (4)$$

where α, β are Cartesian components, μ is the chemical potential of electrons (the Fermi level), V is volume of the unit cell, e is electronic charge, ε is the band eigenvalue, $v_{\alpha}(i, \mathbf{k})$ is the electron group velocity, and $f_{\mu}(T, \varepsilon)$ is the Fermi–Dirac distribution.

The carrier relaxation time (τ_e) under the electron–phonon averaged (EPA) approximation was evaluated using the following equation [33]:

$$\tau_e^{-1}(\varepsilon, \mu, T) = \frac{2\pi\Omega}{g_s \hbar} \sum_v \left\{ g_v^2(\varepsilon, \varepsilon + \bar{\omega}v) [n(\bar{\omega}v, T) + f(\varepsilon + \bar{\omega}v, \mu, T)] \times \rho(\varepsilon + \bar{\omega}v) + g_v^2(\varepsilon, \varepsilon - \bar{\omega}v) [n(\bar{\omega}v, T) + 1 - f(\varepsilon - \bar{\omega}v, \mu, T)] \rho(\varepsilon - \bar{\omega} * v) \right\} \quad (5)$$

Here, ε is the energy of the carriers, μ is the chemical potential, Ω is the volume of the primitive unit cell, $\hbar$ is the reduced Planck's constant, g_s is the spin degeneracy, v is the phonon mode index, g_v^2 is the averaged electron–phonon matrix, $\bar{\omega}v$ is the averaged phonon mode energy, $n(\bar{\omega}v, T)$ is the Bose–Einstein distribution function, $f(\varepsilon + \bar{\omega}v, \mu, T)$ is the Fermi–Dirac distribution function, and ρ is the density of states per unit energy and unit volume.

The lattice thermal conductivity, κ_l , is computed using the Boltzmann transport equation integrated within the ShengBTE code [34], incorporating second- and third-order interatomic force constants (IFCs). The lattice thermal conductivity component $\kappa_l^{\alpha\beta}$ (α, β represents three Cartesian axes) is given by

$$\kappa_l^{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_{\lambda} f_0(f_0 + 1) (\hbar \omega_{\lambda})^2 v_{\lambda}^{\alpha} v_{\lambda}^{\beta} \tau_{\lambda}^0 \quad (6)$$

where Ω , N , f_0 , ω_{λ} , v_{λ} , and τ_{λ}^0 are volume, number of phonon vectors, Bose–Einstein distribution function, frequency, group velocity, and lifetime of phonon mode λ , respectively. The second-order and third-order IFCS were calculated by a $2 \times 2 \times 2$ supercell, including 128 atoms. The third-order IFCS took the 5th nearest neighbor into consideration. The grid mesh for the phonon was set to $20 \times 20 \times 20$ to obtain convergent lattice thermal conductivity.

3. Results and Discussion

3.1. Electronic Properties

CdX adopts a zincblende, sphalerite structure and crystallizes in the cubic $F4\bar{3}m$ space group, as depicted in Figure 1a,d. Each X^{2-} ion is bonded to four equivalent Cd^{2+} atoms to form corner-sharing XCd_4 tetrahedra. To facilitate our study, we constructed a $2 \times 2 \times 2$ supercell of CdX , denoted as Cd_8X_8 as shown in Figure 1b,e, and replaced one X atom. The resulting doped structures are illustrated in Figure 1c,f. The relaxed lattice constants are also given in Figure 1. The lattice constant and bond length of Cd_8Te_8 are longer than those of Cd_8Se_8 , indicating a stronger bond strength in Cd – Se . Upon doping, the lattice constant of Cd_8Se_7Te increases, while that of Cd_8Te_7Se decreases.

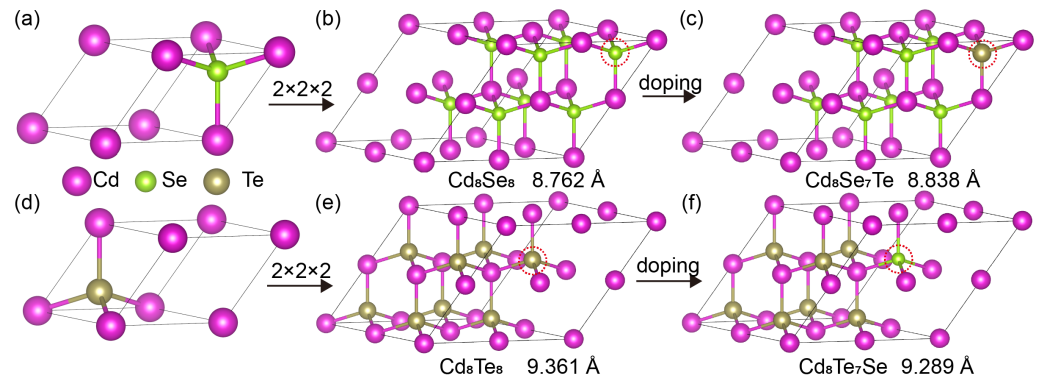


Figure 1. The unit cell of (a) *CdSe* and (d) *CdTe*. The $2 \times 2 \times 2$ supercell of (b) *Cd₈Se₈* and (e) *Cd₈Te₈*. The doped structures of (c) *Cd₈Se₇Te* and (f) *Cd₈Te₇Se*.

The band structures depicted in Figure 2a–f all display a similar band shape, with the only distinguishing factor being the band gap. It is evident that the band structures obtained from the HSE06 method exhibit a similar shape to those obtained from the PBE method, with notable differences observed in the band gaps. Specifically, the band gaps for *CdSe* and *CdTe* computed using the PBE method are reported as 0.47 eV and 0.58 eV, respectively, whereas those computed using the HSE06 method are reported as 1.42 eV and 1.34 eV, respectively. These findings closely align with the results reported in Ref. [35]. Following doping, there is a reduction in the band gaps. In the case of *Cd₈Se₇Te*, the band gap reduced to 0.372 eV, and for *Cd₈Te₇Se*, it reduced to 0.441 eV. Notably, both the valence band maximum (VBM) and conduction band minimum (CBM) are situated at the Γ point. Furthermore, the valence band demonstrates multiple valleys. Similar trends in band structure changes have been observed in other isovalent doped systems [36]. The relationship between band gaps and composition in these systems can be characterized by the quadratic Vegard's law as [36]

$$E_g^{A_{1-x}B_x}(x) = (1-x)E_g^A + xE_g^B - bx(1-x) \quad (7)$$

where E_g^A and E_g^B are the band gaps of the host materials, *A* and *B*, respectively, *x* is the composition, and *b* is a bowing parameter. In our case, *A* and *B* represent *CdSe* and *CdTe*, respectively, with *x* equal to 1/8. By fitting bowing parameter *b*, we found it to be 1.037 eV for *Cd₈Se₇Te*. *b* through *Cd₈Se₇Te* is 1.037 eV. Subsequently, we applied this model and fitted *b* to *Cd₈Te₇Se* and obtained a band gap of 0.453 eV, which closely aligns with the calculated value. This suggests that the band gap of doped *CdX* can be predicted using Vegard's law.

To gain a comprehensive understanding of the band structure, we present the projected band structures of *Cd₈Se₇Te* and *Cd₈Te₇Se* in Figure 3. The dot size in the projected band structure represents the contribution of corresponding orbitals. The conduction band is primarily composed of the 5 *s* orbitals of *Cd*. For *CdX* or doped *CdX*, their conduction band is the same, while the valence band is dominated by the *p* and *d* orbitals of all atoms. Notably, both *Se* and *Te* atoms demonstrate similar contributions, with the *s* orbitals of *Se* being a little stronger than those of *Te*, and the *p* orbitals of *Se* being a little weaker than those of *Te*. Although isovalent atoms contribute to the band structure, their effect is relatively subtle.

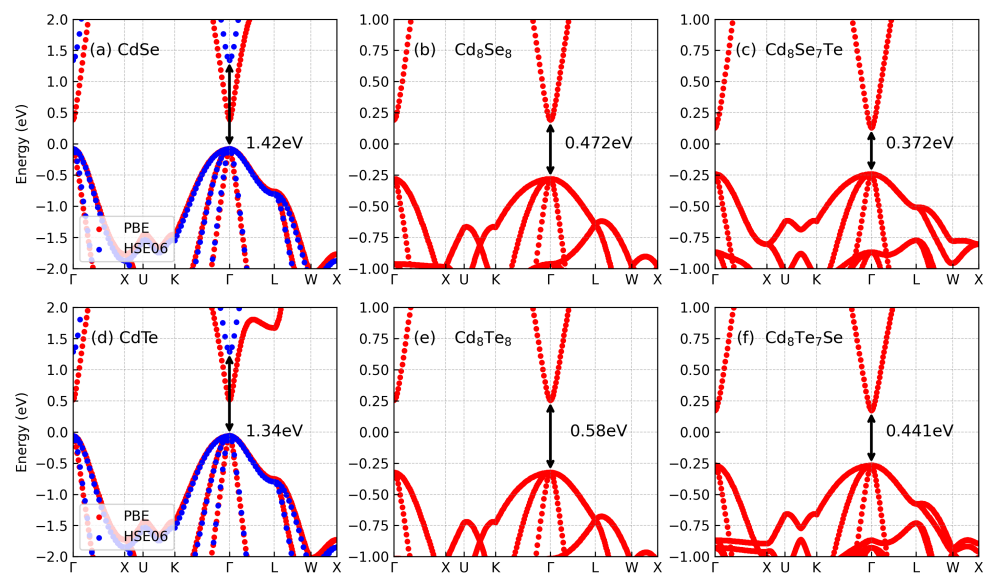


Figure 2. The band structures of (a) CdSe , (b) Cd_8Se_8 , (c) $\text{Cd}_8\text{Se}_7\text{Te}$, (d) CdSe , (e) Cd_8Se_8 , and (f) $\text{Cd}_8\text{Se}_7\text{Te}$.

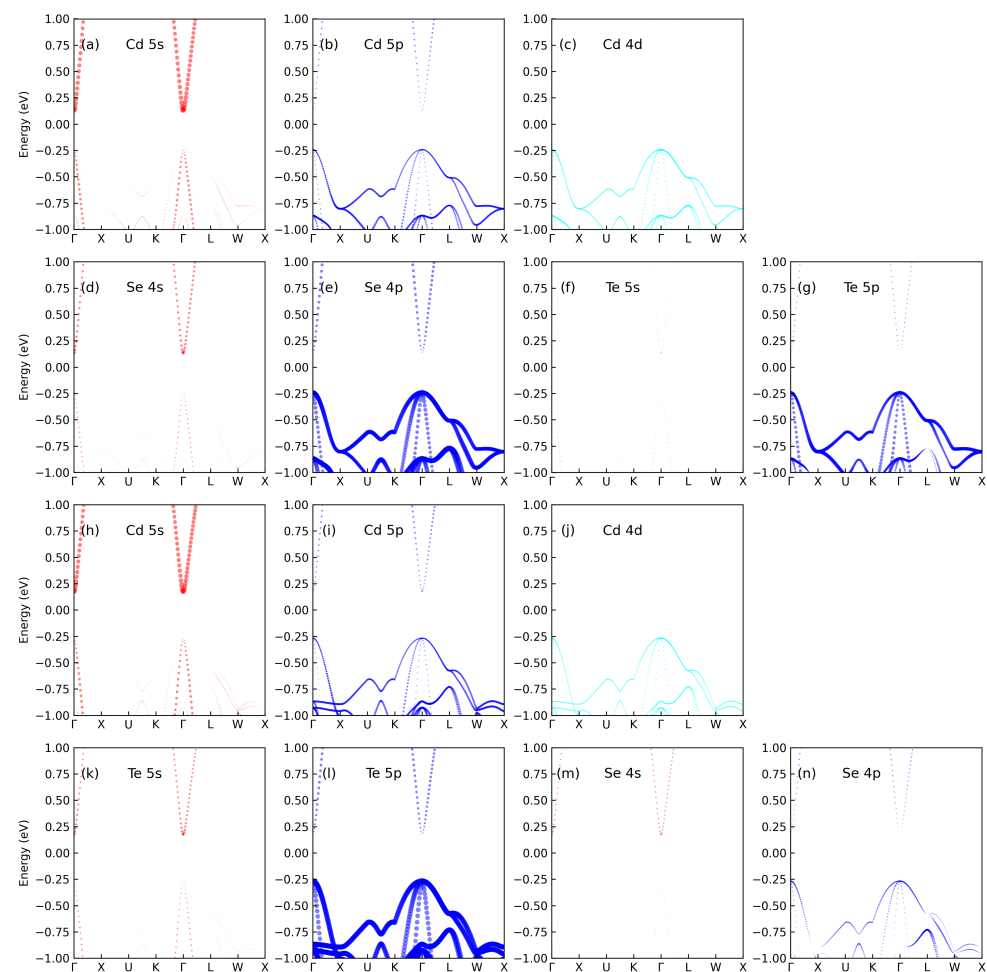


Figure 3. The projected band structure of (a) $\text{Cd } 5s$, (b) $\text{Cd } 5p$, (c) $\text{Cd } 4d$, (d) $\text{Se } 4s$, (e) $\text{Se } 4p$, (f) $\text{Te } 5s$, and (g) $\text{Te } 5p$ of $\text{Cd}_8\text{Se}_7\text{Te}$. The projected band structure of (h) $\text{Cd } 5s$, (i) $\text{Cd } 5p$, (j) $\text{Cd } 4d$, (k) $\text{Te } 5s$, (l) $\text{Te } 5p$, (m) $\text{Se } 4s$, and (n) $\text{Se } 4p$ of $\text{Cd}_8\text{Te}_7\text{Se}$.

Figure 4 illustrates the calculated values of S , σ , and $S^2\sigma$ at 300 K for different carrier concentrations. Generally, S can be expressed as [37]

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad (8)$$

in which k_B , e , m^* , and h are the Boltzmann constant, electron charge, effective mass, and Planck constant, respectively. Analysis of Figure 4a,d reveals that the absolute values of S all decrease as the carrier concentration increases. Due to their similar band curvatures (m^*), CdX exhibits comparable S values. Notably, the S for hole doping (p-type) is significantly higher than that for electron doping (n-type). For instance, p-type S can reach 400 $\mu\text{V/K}$, while n-type S is only 100 $\mu\text{V/K}$ at 10^{19} cm^{-3} . This difference can be attributed to the valence band having a much sharper curvature and a larger m^* compared to the conduction band. The behavior of σ as a function of carrier concentration is depicted in Figure 4b,e. In contrast to S , all σ values increase as the carrier concentration rises. N-type σ is higher than p-type σ , especially at low carrier concentrations. When the carrier concentration reaches to 10^{20} – 10^{21} cm^{-3} , both n-type and p-type σ reach the 10^5 S/m level. Due to the Wiedemann–Franz relation [38], κ_e exhibits a linear correlation with σ ; hence, there is no need to separately display κ_e . In Ref. [39], the electrical parameters of various thin film CdSe samples were investigated. The carrier concentration of thin film CdSe was found to be approximately (10^{20} cm^{-3}) with a Seebeck coefficient of around ($-50 \mu\text{V/K}$). Our obtained value of ($-25 \mu\text{V/K}$) aligns closely with this result. It is worth noting that our calculated electrical conductivity (10^5 S/m) significantly exceeds the experimental value (10^2 S/m). This discrepancy can be attributed to the DFT simulation assuming a perfect crystal structure, while experimental samples typically exhibit boundaries, grain effects, and scattering mechanisms that substantially reduce the electrical conductivity.

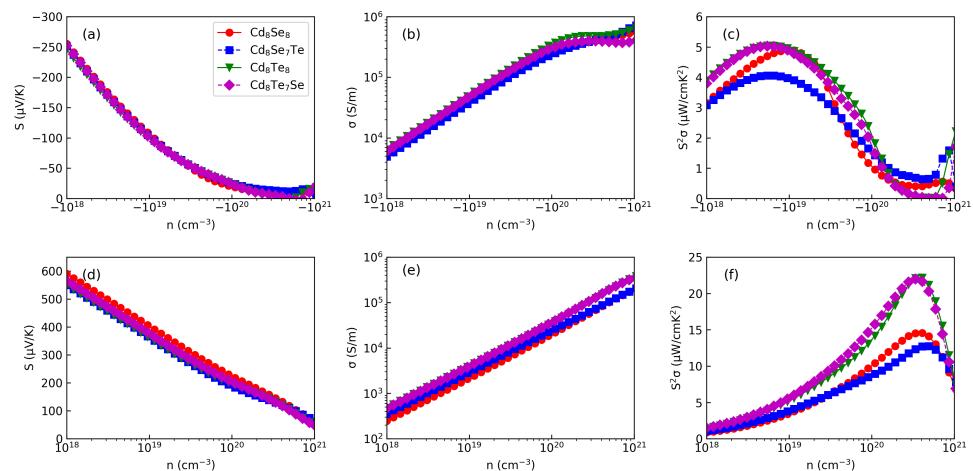


Figure 4. The electronic transport properties of (a,d) S , and (b,e) σ , and (c,f) $S^2\sigma$.

When considering S and σ , it is evident that the n-type $S^2\sigma$ is significantly lower than p-type $S^2\sigma$, as depicted in Figure 4e,f. The optimized carrier concentrations for n-type and p-type are determined to be 10^{19} and $5 \times 10^{20} \text{ cm}^{-3}$, respectively. All CdX materials exhibit similar n-type $S^2\sigma$ values around 4–5 $\mu\text{W/cmK}^2$. The maximum n-type $S^2\sigma$ for $CdTe$ (20 $\mu\text{W/cmK}^2$) is twice as much as that of $CdSe$ (10 $\mu\text{W/cmK}^2$). The p-type $S^2\sigma$ value of CdX is comparable to well-known thermoelectric materials such as Cu_2Se [40] and SnSe [41], indicating their superior p-type thermoelectric properties. This analysis implies that doping can effectively maintain the electronic transport properties of CdX .

3.2. Phononic Properties

Next, we shift our focus to the phonon dispersion in Figure 5. In the low-frequency range, all structures exhibit similar phonon dispersions, as depicted in Figure 5a,c,e,g. All

structures show non-negative values in their phonon dispersions, confirming their stability. Upon doping *Te* atoms into Cd_8Se_8 , phonon modes around 130 cm^{-1} moving to a higher frequency. However, for Cd_8Te_8 , doping *Se* atoms leads to phonon modes around 175 cm^{-1} moving to lower frequency. This phenomenon can be seen more clearly in the phonon DOS in Figure 5b,d,f,h. In the phonon DOS, there are two peaks around 130 cm^{-1} in Cd_8Se_8 . After doping *Te* atoms, the peak around 130 cm^{-1} disappears and new peaks at 150 cm^{-1} arise. From the projected phonon DOS, it is evident that the new peaks at 150 cm^{-1} are contributed by *Te* atoms. The case for Cd_8Te_8 is similar. When doping *Se* atoms, the peak around 175 cm^{-1} disappears and new peaks contributed by *Se* atoms at 150 cm^{-1} arise. An increase in the strength of interatomic bonds leads to an increase in the vibration frequency near the atom's position [42,43].

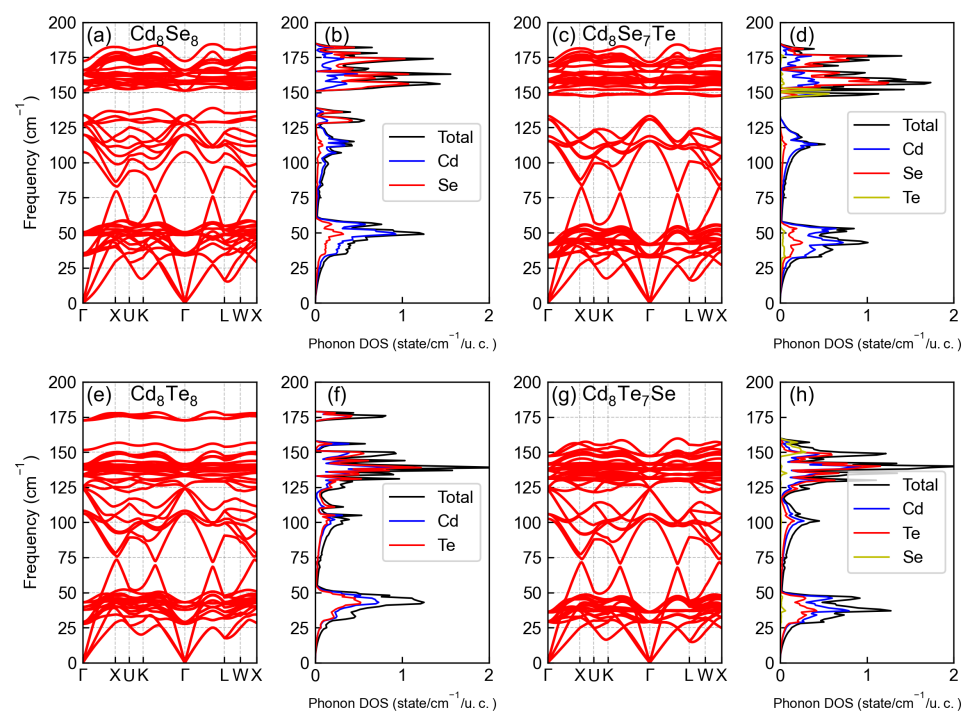


Figure 5. The phonon dispersions for (a) Cd_8Se_8 , (c) $\text{Cd}_8\text{Se}_7\text{Te}$, (e) Cd_8Te_8 , and (g) $\text{Cd}_8\text{Te}_7\text{Se}$. The total and projected phononic density of states for (b) Cd_8Se_8 , (d) $\text{Cd}_8\text{Se}_7\text{Te}$, (f) Cd_8Te_8 , and (h) $\text{Cd}_8\text{Te}_7\text{Se}$.

We further investigate the thermal transport properties of CdX and their corresponding doping systems. Figure 6a shows κ_l at different temperatures. κ_l decreases with temperature due to stronger phonon–phonon scattering. Cd_8Se_8 exhibit lower κ_l values than Cd_8Te_8 , as stronger bonds tend to transfer more heat, leading to higher thermal conductivity in crystal structures with stronger bonds. After doping, κ_l is reduced. Specifically, the κ_l of $\text{Cd}_8\text{Se}_7\text{Te}$ is much lower than that of $\text{Cd}_8\text{Te}_7\text{Se}$, with the former being $0.5\text{ Wm}^{-1}\text{K}^{-1}$ and the latter being $0.8\text{ Wm}^{-1}\text{K}^{-1}$ at 300 K. Furthermore, we illustrate the cumulative κ_l as a function of frequency at 300 K in Figure 6b. For undoped CdX , the rate of increase in κ_l begins to decrease at 75 cm^{-1} , while the node at which the rate of increase slows down after doping drops to 50 cm^{-1} . This indicates that doping not only reduces κ_l , but also lowers the frequency at which the maximum rate of κ_l increase occurs, further contributing to the reduction in κ_l .

To further elucidate the reasons for the behavior of κ_l , we calculate the phonon group velocity (v_g), phonon lifetime (τ_{ph}), and Grüneisen parameter (γ) as a function of frequency at 300 K as shown in Figure 7. In thermal transport, γ represents the sensitivity of a material's phonon frequency to changes in volume or pressure, providing insight into the strength of anharmonic scattering. A large value of $|\gamma|$ indicates the potential for strong phonon–phonon anharmonic scattering [44]. From Figure 7a–d, it can be observed that

the doped v_g remain largely unchanged, especially in the low-frequency region, consistent with the earlier phonon spectral variations. The speed at which energy is propagated through a material's lattice vibrations correlates with the distribution of vibrational modes across different frequencies. After doping, a significant decrease in the low-frequency τ_{ph} is observed in Figure 7e–h. Figure 6b indicates that thermal conductivity is primarily influenced by low-frequency phonons. Subsequently, we analyze the γ in Figure 7i–l, which describes the strength of anharmonic scattering. It is found that the γ also decreases, indicating an enhancement in the strength of anharmonic scattering. This phenomenon evidently arises from the presence of dopant elements.

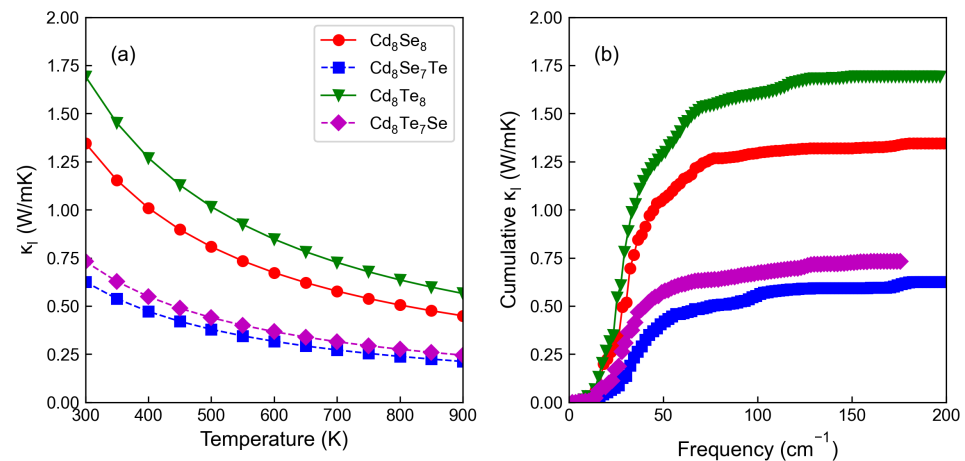


Figure 6. (a) The lattice thermal conductivity as a function of temperature. (b) Cumulative lattice thermal conductivity as a function of frequency at 300 K.

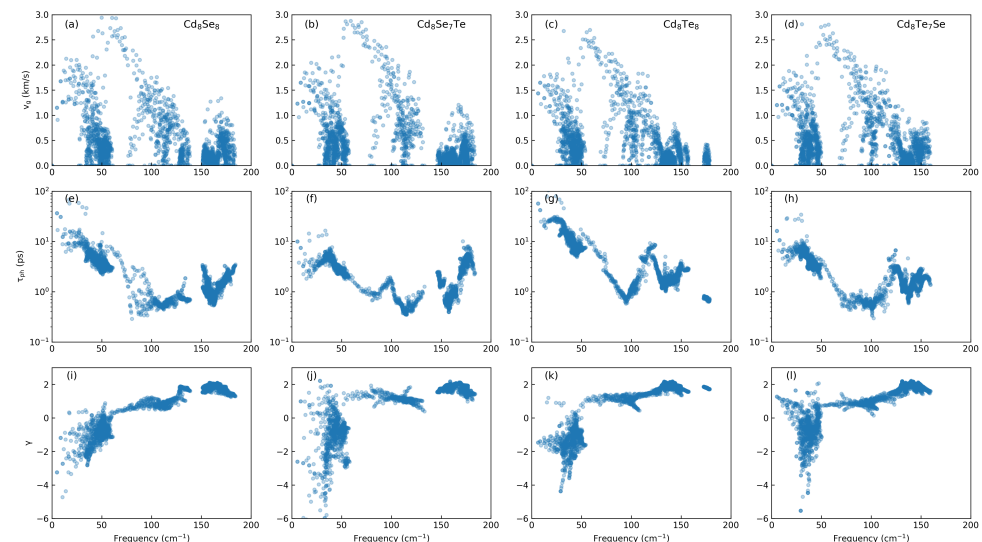


Figure 7. The (a–d) phonon group velocity, (e–h) phonon lifetime, and (i–l) Grüneisen parameter as a function of frequency at 300 K.

3.3. Mechanical Properties and Bonding Analysis

Figure 8a illustrates the calculated Young's modulus and shear modulus. It is evident that both Young's modulus and shear modulus gradually decrease with an increase in the ratio of *Te* content. These mechanical properties are indicative of the averaged bonding strength within the material. As the *Te* content increases, the averaged bonding strength of *CdX* diminishes. Furthermore, we conduct a comprehensive analysis of the bonding in *CdX* using the COHP method, as depicted in Figure 8b,c. In this context, negative COHP values indicate bonding states, while positive COHP values indicate antibonding states.

It is noteworthy that all structures exhibit a similar COHP phenomenon. Upon doping, states for *Cd–Se* in *Cd₈Te₇Se* and *Cd–Te* in *Cd₈Se₇Te* exhibit slightly enhanced strength compared to pristine states. Doping introduces new antibonding states. Below the Fermi level, bonding and antibonding states appear alternately. Notably, bonding states are stronger than antibonding states, thus ensuring the stability of the structure. Additionally, antibonding states typically possess higher energy levels than bonding states, contributing to a reduction in thermal conductivity [45]. This phenomenon arises from the greater delocalization of electrons in antibonding states, which results in reduced heat-carrying capacity compared to bonding states. Consequently, this accounts for the relatively low lattice thermal conductivity observed in *CdX*.

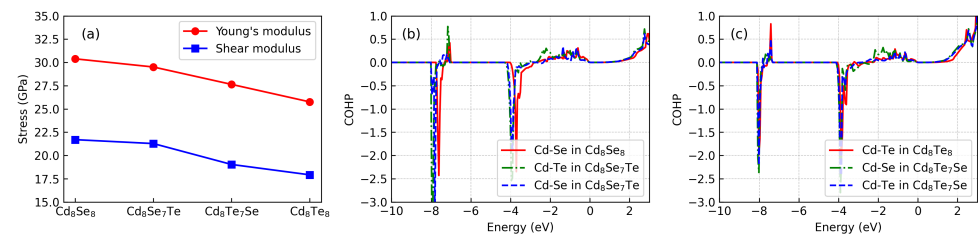


Figure 8. (a) Elastic properties for *CdX*. COHP for (b) *Cd₈Se₇Te* and (c) *Cd₈Te₇Se*.

3.4. Thermoelectric Properties

Figure 9 illustrates maximum $S^2\sigma$ and ZT values at different temperatures. The $S^2\sigma_{max}$ values for doped and pristine *CdX* are comparable across temperature ranges as shown in Figure 9a,b. As temperature increases, the n-type $S^2\sigma_{max}$ values exhibit further enhancement, with $S^2\sigma_{max}$ reaching $9.8 \mu\text{W}/\text{cm}^2$ at 900 K for *Cd₈Se₇Te*. In contrast, there is no clear increasing trend observed for p-type $S^2\sigma_{max}$. P-type $S^2\sigma_{max}$ values are much higher than n-type ones. Notably, for *Cd₈Te₈* and *Cd₈Te₇Se*, p-type $S^2\sigma_{max}$ is approximately $25 \mu\text{W}/\text{cm}^2$, while for *Cd₈Se₈* and *Cd₈Se₇Te*, it is around $15 \mu\text{W}/\text{cm}^2$. Doping does not degrade the $S^2\sigma_{max}$ for *CdX*, as indicated by our findings.

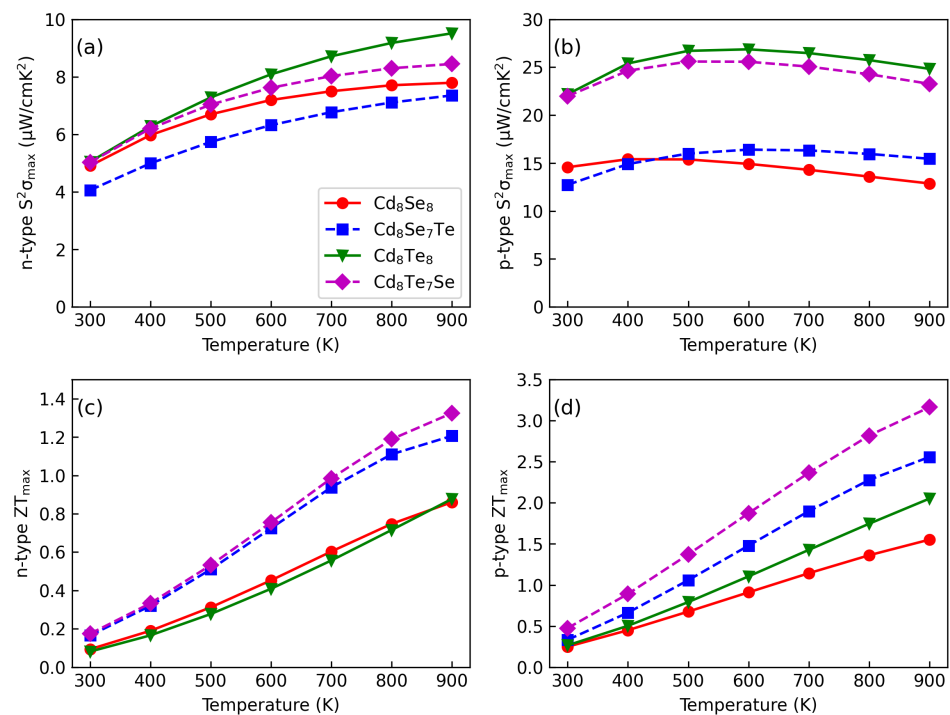


Figure 9. The maximum (a) n-type, (b) p-type $S^2\sigma$ and (c) n-type, (d) p-type ZT values as a function of temperatures.

When combined with electronic and phononic transport properties, the ZT_{max} values listed in Figure 9c,d demonstrate high thermoelectric performance for CdX at high temperatures. Despite the lack of increase in n-type $S^2\sigma_{max}$ with temperature, there is lower lattice thermal conductivity with temperatures resulting in higher ZT_{max} values for doped systems compared to pristine ones. Furthermore, these values can be further enhanced with increasing temperature, with p-type ZT_{max} values reaching up to 3.13 at 900 K. Our results suggest that doped CdX ($X = Te, Se$) presents potential for realizing both n-type and p-type thermoelectric materials for high-temperature applications.

4. Conclusions

In this study, we investigated the electronic, carrier, phonon transport, and thermoelectric properties of isovalent doped CdX ($X = Te, Se$) compounds using first-principles calculations with the Boltzmann transport equation. Due to the similar properties of Te and Se , the band structures remain nearly unchanged except for the band gaps in doped CdX . The bandgaps are 0.472 eV, 0.372 eV, 0.58 eV, and 0.441 eV for Cd_8Se_8 , Cd_8Se_7Te , Cd_8Te_8 , and Cd_8Te_7Se , respectively. Electronic transport properties of CdX are comparable for doped and pristine compounds. However, doping significantly reduces lattice thermal conductivity due to the introduction of impurity scattering. The maximum p-type (n-type) ZT values at 900 K are 1.5 (0.84), 2.51 (1.21), 2.1 (0.88), and 3.13 (1.33) for Cd_8Se_8 , Cd_8Se_7Te , Cd_8Te_8 , and Cd_8Te_7Se , respectively. Our study focuses on investigating the impact of isovalent doping in enhancing the thermoelectric properties of materials. Isovalent doping, such as with selenides and tellurides, can maintain electronic transport properties while effectively scattering phonons and decreasing lattice thermal conductivity. Future investigations could explore the potential of decoupling thermoelectric properties through homoelement doping.

Author Contributions: J.J.: Calculations, Formal analysis, Writing—original draft. F.L.: Review and editing. W.C.: Calculations, Review and editing. Z.W.: Funding acquisition, Supervision, Project administration. All authors have read and agreed to the published version of the manuscript.

Funding: The authors of this work acknowledge the National Natural Science Foundation of China (Grant No. 12122408, 12074292), and the Fundamental Research Funds for the Central Universities (Grant No. 2042023kf0109).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data provided in this study could be released upon reasonable request.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Zoui, M.A.; Bentouba, S.; Stocholm, J.G.; Bourouis, M. A Review on Thermoelectric Generators: Progress and Applications. *Energies* **2020**, *13*, 3606. [\[CrossRef\]](#)
2. Sootsman, J.R.; Chung, D.Y.; Kanatzidis, M.G. New and Old Concepts in Thermoelectric Materials. *Angew. Chem. Int. Ed.* **2009**, *48*, 8616–8639. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Shi, X.L.; Zou, J.; Chen, Z.G. Advanced Thermoelectric Design: From Materials and Structures to Devices. *Chem. Rev.* **2020**, *120*, 7399–7515. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Zhao, W.; Ding, J.; Zou, Y.; Di, C.a.; Zhu, D. Chemical doping of organic semiconductors for thermoelectric applications. *Chem. Soc. Rev.* **2020**, *49*, 7210–7228. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Zheng, Z.H.; Shi, X.L.; Ao, D.W.; Liu, W.D.; Chen, Y.X.; Li, F.; Chen, S.; Tian, X.Q.; Li, X.R.; Duan, J.Y.; et al. Rational band engineering and structural manipulations inducing high thermoelectric performance in n-type $CoSb_3$ thin films. *Nano Energy* **2021**, *81*, 105683. [\[CrossRef\]](#)
6. Hooshmand Zaferani, S.; Ghomashchi, R.; Vashae, D. Strategies for engineering phonon transport in Heusler thermoelectric compounds. *Renew. Sustain. Energy Rev.* **2019**, *112*, 158–169. [\[CrossRef\]](#)
7. Novak, T.G.; Kim, K.; Jeon, S. 2D and 3D nanostructuring strategies for thermoelectric materials. *Nanoscale* **2019**, *11*, 19684–19699. [\[CrossRef\]](#) [\[PubMed\]](#)

8. Slade, T.J.; Pal, K.; Grovogui, J.A.; Bailey, T.P.; Male, J.; Khoury, J.F.; Zhou, X.; Chung, D.Y.; Snyder, G.J.; Uher, C.; et al. Contrasting SnTe-NaSbTe₂ and SnTe-NaBiTe₂ Thermoelectric Alloys: High Performance Facilitated by Increased Cation Vacancies and Lattice Softening. *J. Am. Chem. Soc.* **2020**, *142*, 12524–12535. [[CrossRef](#)] [[PubMed](#)]
9. Liu, Z.; Cheng, H.; Le, Q.; Chen, R.; Li, J.; Ouyang, J. Giant Thermoelectric Properties of Ionogels with Cationic Doping. *Adv. Energy Mater.* **2022**, *12*, 2200858. [[CrossRef](#)]
10. Perumal, S.; Samanta, M.; Ghosh, T.; Shenoy, U.S.; Bohra, A.K.; Bhattacharya, S.; Singh, A.; Waghmare, U.V.; Biswas, K. Realization of High Thermoelectric Figure of Merit in GeTe by Complementary Co-doping of Bi and In. *Joule* **2019**, *3*, 2565–2580. [[CrossRef](#)]
11. Chen, C.; Jacobs, I.E.; Kang, K.; Lin, Y.; Jellett, C.; Kang, B.; Lee, S.B.; Huang, Y.; BaloochQarai, M.; Ghosh, R.; et al. Observation of Weak Counterion Size Dependence of Thermoelectric Transport in Ion Exchange Doped Conducting Polymers Across a Wide Range of Conductivities. *Adv. Energy Mater.* **2023**, *13*, 2202797. [[CrossRef](#)]
12. Zhao, W.; Jin, K.; Fu, L.; Shi, Z.; Xu, B. Mass Production of Pt Single-Atom-Decorated Bismuth Sulfide for n-Type Environmentally Friendly Thermoelectrics. *Nano Lett.* **2022**, *22*, 4750–4757. [[CrossRef](#)]
13. Van Du, N.; Rahman, J.U.; Huy, P.T.; Shin, W.H.; Seo, W.S.; Kim, M.H.; Lee, S. X-site aliovalent substitution decoupled charge and phonon transports in XYZ half-Heusler thermoelectrics. *Acta Mater.* **2019**, *166*, 650–657. [[CrossRef](#)]
14. Han, S.; Dai, S.; Ma, J.; Ren, Q.; Hu, C.; Gao, Z.; Duc Le, M.; Sheptyakov, D.; Miao, P.; Torii, S.; et al. Strong phonon softening and avoided crossing in aliovalence-doped heavy-band thermoelectrics. *Nat. Phys.* **2023**, *19*, 1649–1657. [[CrossRef](#)]
15. Baranets, S.; Balvanz, A.; Darone, G.M.; Bobev, S. On the Effects of Aliovalent Substitutions in Thermoelectric Zintl Pnictides. Varied Polyanionic Dimensionality and Complex Structural Transformations—The Case of Sr₃ZnP₃ vs. Sr₃AlxZn_{1-x}P₃. *Chem. Mater.* **2022**, *34*, 4172–4185. [[CrossRef](#)]
16. Musah, J.D.; Ilyas, A.M.; Venkatesh, S.; Mensah, S.; Kwofie, S.; Roy, V.A.L.; Wu, C.M.L. Isovalent substitution in metal chalcogenide materials for improving thermoelectric power generation—A critical review. *Nano Res. Energy* **2022**, *1*, e9120034. [[CrossRef](#)]
17. Lee, K.H.; Kim, H.S.; Kim, M.; Roh, J.W.; Lim, J.H.; Kim, W.J.; Kim, S.-i.; Lee, W. Isovalent sulfur substitution to induce a simultaneous increase in the effective mass and weighted mobility of a p-type Bi–Sb–Te alloy: An approach to enhance the thermoelectric performance over a wide temperature range. *Acta Mater.* **2021**, *205*, 116578. [[CrossRef](#)]
18. He, X.; Zhang, H.; Nose, T.; Katase, T.; Tadano, T.; Ide, K.; Ueda, S.; Hiramatsu, H.; Hosono, H.; Kamiya, T. Degenerated Hole Doping and Ultra-Low Lattice Thermal Conductivity in Polycrystalline SnSe by Nonequilibrium Isovalent Te Substitution. *Adv. Sci.* **2022**, *9*, 2105958. [[CrossRef](#)]
19. Gao, B.; Tang, J.; Meng, F.; Li, W. Band manipulation for high thermoelectric performance in SnTe through heavy CdSe-alloying. *J. Mater.* **2019**, *5*, 111–117. [[CrossRef](#)]
20. Tao, Q.; Deng, R.; Li, J.; Yan, Y.; Su, X.; Poudeu, P.F.P.; Tang, X. Enhanced Thermoelectric Performance of Bi_{0.46}Sb_{1.54}Te₃ Nanostructured with CdTe. *ACS Appl. Mater. Interfaces* **2020**, *12*, 26330–26341. [[CrossRef](#)]
21. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G.L.; Cococcioni, M.; Dabo, I.; et al. Quantum ESPRESSO: A modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter* **2009**, *21*, 395502. [[CrossRef](#)] [[PubMed](#)]
22. Giannozzi, P.; Andreussi, O.; Brumme, T.; Bunau, O.; Nardelli, M.B.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Cococcioni, M.; et al. Advanced capabilities for materials modelling with Quantum ESPRESSO. *J. Phys. Condens. Matter* **2017**, *29*, 465901. [[CrossRef](#)] [[PubMed](#)]
23. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. [[CrossRef](#)] [[PubMed](#)]
24. Prandini, G.; Marrazzo, A.; Castelli, I.E.; Mounet, N.; Marzari, N. Precision and efficiency in solid-state pseudopotential calculations. *NPJ Comput. Mater.* **2018**, *4*, 72. [[CrossRef](#)]
25. Heyd, J.; Scuseria, G.E.; Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* **2003**, *118*, 8207–8215. [[CrossRef](#)]
26. Krukau, A.V.; Vydrov, O.A.; Izmaylov, A.F.; Scuseria, G.E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.* **2006**, *125*, 224106. [[CrossRef](#)] [[PubMed](#)]
27. Maintz, S.; Deringer, V.L.; Tchougréeff, A.L.; Dronskowski, R. Analytic projection from plane-wave and PAW wavefunctions and application to chemical-bonding analysis in solids. *J. Comput. Chem.* **2013**, *34*, 2557–2567. [[CrossRef](#)] [[PubMed](#)]
28. Maintz, S.; Deringer, V.L.; Tchougréeff, A.L.; Dronskowski, R. LOBSTER: A tool to extract chemical bonding from plane-wave based DFT. *J. Comput. Chem.* **2016**, *37*, 1030–1035. [[CrossRef](#)] [[PubMed](#)]
29. Hill, R. The Elastic Behaviour of a Crystalline Aggregate. *Proc. Phys. Soc. Sect. A* **1952**, *65*, 349. [[CrossRef](#)]
30. Yalameha, S.; Nourbakhsh, Z.; Vashae, D. ElATools: A tool for analyzing anisotropic elastic properties of the 2D and 3D materials. *Comput. Phys. Commun.* **2022**, *271*, 108195. [[CrossRef](#)]
31. Momma, K.; Izumi, F. VESTA: A three-dimensional visualization system for electronic and structural analysis. *J. Appl. Crystallogr.* **2008**, *41*, 653–658. [[CrossRef](#)]
32. Madsen, G.K.; Singh, D.J. BoltzTraP. A code for calculating band-structure dependent quantities. *Comput. Phys. Commun.* **2006**, *175*, 67–71. [[CrossRef](#)]
33. Samsonidze, G.; Kozinsky, B. Accelerated Screening of Thermoelectric Materials by First-Principles Computations of Electron–Phonon Scattering. *Adv. Energy Mater.* **2018**, *8*, 1800246. [[CrossRef](#)]

34. Li, W.; Carrete, J.; Katcho, N.A.; Mingo, N. ShengBTE: A solver of the Boltzmann transport equation for phonons. *Comput. Phys. Commun.* **2014**, *185*, 1747–1758. [[CrossRef](#)]
35. Gopal, P.; Fornari, M.; Curtarolo, S.; Agapito, L.A.; Liyanage, L.S.I.; Nardelli, M.B. Improved predictions of the physical properties of Zn- and Cd-based wide band-gap semiconductors: A validation of the ACBN0 functional. *Phys. Rev. B* **2015**, *91*, 245202. [[CrossRef](#)]
36. Polak, M.P.; Scharoch, P.; Kudrawiec, R. The effect of isovalent doping on the electronic band structure of group IV semiconductors. *J. Phys. Appl. Phys.* **2020**, *54*, 085102. [[CrossRef](#)]
37. Snyder, G.J.; Toberer, E.S. Complex thermoelectric materials. *Nat. Mater.* **2008**, *7*, 105–114. [[CrossRef](#)] [[PubMed](#)]
38. Yadav, A.; Deshmukh, P.; Roberts, K.; Jisrawi, N.; Valluri, S. An analytic study of the Wiedemann–Franz law and the thermoelectric figure of merit. *J. Phys. Commun.* **2019**, *3*, 105001. [[CrossRef](#)]
39. Ahamed, S.T.; Kulsi, C.; Kirti,.; Banerjee, D.; Srivastava, D.N.; Mondal, A. Synthesis of multifunctional CdSe and Pd quantum dot decorated CdSe thin films for photocatalytic, electrocatalytic and thermoelectric applications. *Surfaces Interfaces* **2021**, *25*, 101149. [[CrossRef](#)]
40. Cao, W.; Wang, Z.; Miao, L.; Shi, J.; Xiong, R. Thermoelectric Properties of Strained β -Cu₂Se. *ACS Appl. Mater. Interfaces* **2021**, *13*, 34367–34373. [[CrossRef](#)]
41. Cao, W.; Wang, Z.; Miao, L.; Shi, J.; Xiong, R. Extremely Anisotropic Thermoelectric Properties of SnSe Under Pressure. *Energy Environ. Mater.* **2023**, *6*, e12361. [[CrossRef](#)]
42. Huang, L.F.; Zeng, Z. Roles of Mass, Structure, and Bond Strength in the Phonon Properties and Lattice Anharmonicity of Single-Layer Mo and W Dichalcogenides. *J. Phys. Chem. C* **2015**, *119*, 18779–18789. [[CrossRef](#)]
43. Yang, X.X.; Li, J.W.; Zhou, Z.F.; Wang, Y.; Yang, L.W.; Zheng, W.T.; Sun, C.Q. Raman spectroscopic determination of the length, strength, compressibility, Debye temperature, elasticity, and force constant of the C-C bond in graphene. *Nanoscale* **2012**, *4*, 502–510. [[CrossRef](#)] [[PubMed](#)]
44. Delaire, O.; Ma, J.; Marty, K.; May, A.F.; McGuire, M.A.; Du, M.H.; Singh, D.J.; Podlesnyak, A.; Ehlers, G.; Lumsden, M.D.; et al. Giant anharmonic phonon scattering in PbTe. *Nat. Mater.* **2011**, *10*, 614–619. [[CrossRef](#)]
45. Kundu, A.; Ma, J.; Carrete, J.; Madsen, G.K.H.; Li, W. Anomalously large lattice thermal conductivity in metallic tungsten carbide and its origin in the electronic structure. *Mater. Today Phys.* **2020**, *13*, 100214. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.