NaInX$_2$ ($X = S$, Se) layered materials for energy harvesting applications: first-principles insights into optoelectronic and thermoelectric properties

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ABSTRACT

In recent times, layered chalcogenide semiconductors have attracted great interest in energy harvesting device applications. In the present study, the structural, electronic, optical and thermoelectric properties of two isostructural chalcogenide materials, NaInS$_2$ and NaInSe$_2$ with hexagonal symmetry ($R$-3$m$) have been studied using the first principles method. A very good agreement has been found between our results with the available experimental and theoretical ones. The studied materials are semiconducting in nature as confirmed from the electronic band structure and optical properties. The strong hybridizations among s orbitals of Na, In and Se atoms push the bottom of the conduction band downward resulting in a narrower band gap of NaInSe$_2$ compared to that of NaInS$_2$ compound. Different optical (dielectric function, photoconductivity, absorption coefficient, reflectivity, refractive index and loss function) and thermoelectric (Seebeck coefficient, electrical conductivity, power factor and thermal conductivity) properties of NaInX$_2$ ($X = S$, Se) have been studied in detail for the first time. It is found that all these properties are significantly anisotropic due to the strongly layered structure of NaInX$_2$ ($X = S$, Se). Strong optical absorption with sharp peaks is found in the far visible to mid ultraviolet (UV) regions while the reflectivity is low in the UV region for both the compounds. Such features indicate feasibility of applications in optoelectronic sector. The calculated thermoelectric power factors at 1000 K for NaInS$_2$ and NaInSe$_2$ along a-axis are found to be 151.5 $\mu$W/cmK$^2$ and 154 $\mu$W/cmK$^2$, respectively.
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0.5, 1.0, 1.5 and 2.0) solid solutions have been synthesized by P. Hu et al. \[6\]. They reported that the NaInS\(_2\) hetero-

1.80–1.88 eV, respectively \[1, 3, 5\]. On the other hand, researchers. Fukuzaki et al. \[1\] have synthesized NaInS\(_2\) (X = S and Se) chalcogenides due to their fascinating structural features, tunable bandgap and unique stoichiometry-controlled electro-optical properties \[3\]. Very recently, layered chalcogenides, NaInS\(_{2-x}\)Se\(_x\) (x = 0, 0.5, 1.0, 1.5 and 2.0) solid solutions have been synthesized by Takahashi et al. \[3\] using ball milling process. The study \[3\] reported that the bandgap of the NaInS\(_2\) compound can be tuned by varying Se content. The experimentally estimated band gap of NaInS\(_{2-x}\)Se\(_x\) (x = 0) is seen to decrease to 2.26 eV when S is replaced completely (x = 1) with Se content. These tunable band gap indicated the potential use of NaInX\(_2\) (X = S and Se) as optoelectronic materials in the visible and even near ultraviolet spectral regions. In addition to this study, NaInS\(_2\) compound and its counterparts have also been studied experimentally and/or theoretically by other researchers. Fukuzaki et al. \[1\] have synthesized NaInX\(_2\)(X = S, O) materials and confirmed the role of anions on the electronic structure using X-ray photoelectron spectroscopy along with first-principles molecular orbital (MO) cluster calculations. The NaInS\(_2\), a heterogeneous nanosheet, was synthesized using a partial cation exchange reaction process by P. Hu et al. \[6\]. They reported that the NaInS\(_2\) heterogeneous nanosheet shows highly improved photocatalytic behavior. It is worth noting that the experimentally and theoretically estimated band gap for NaInS\(_2\) resides in the range 2.30–3.32 eV and 1.80–1.88 eV, respectively \[1, 3, 5\]. On the other hand, the estimated band gap using different theoretical approach for NaInSe\(_2\) lies within the range 1.0–2.26 eV \[3, 9\].

1 Introduction

Ternary chalcogenide semiconductors are considered to be promising materials for various applications such as in photovoltaics, photocatalysts, nonlinear optics, photo-response, and topological insulator applications \[1–9\]. Among the chalcogenide materials, researchers have paid particular attention to ternary indium compounds like NaInX\(_2\) (X = S and Se) chalcogenides due to their fascinating structural features, tunable bandgap and unique stoichiometry-controlled electro-optical properties \[3\]. Very recently, layered chalcogenides, NaInS\(_{2-x}\)Se\(_x\) (x = 0, 0.5, 1.0, 1.5 and 2.0) solid solutions have been synthesized by Takahashi et al. \[3\] using ball milling process. The study \[3\] reported that the bandgap of the NaInS\(_2\) compound can be tuned by varying Se content. The experimentally estimated band gap of NaInS\(_{2-x}\)Se\(_x\) (x = 0) is seen to decrease to 2.26 eV when S is replaced completely (x = 1) with Se content. These tunable band gap indicated the potential use of NaInX\(_2\) (X = S and Se) as optoelectronic materials in the visible and even near ultraviolet spectral regions. In addition to this study, NaInS\(_2\) compound and its counterparts have also been studied experimentally and/or theoretically by other researchers. Fukuzaki et al. \[1\] have synthesized NaInX\(_2\)(X = S, O) materials and confirmed the role of anions on the electronic structure using X-ray photoelectron spectroscopy along with first-principles molecular orbital (MO) cluster calculations. The NaInS\(_2\), a heterogeneous nanosheet, was synthesized using a partial cation exchange reaction process by P. Hu et al. \[6\]. They reported that the NaInS\(_2\) heterogeneous nanosheet shows highly improved photocatalytic behavior. It is worth noting that the experimentally and theoretically estimated band gap for NaInS\(_2\) resides in the range 2.30–3.32 eV and 1.80–1.88 eV, respectively \[1, 3, 5\]. On the other hand, the estimated band gap using different theoretical approach for NaInSe\(_2\) lies within the range 1.0–2.26 eV \[3, 9\].

Recently we have already studied the structural, mechanical and thermodynamic properties in detail of ternary layered chalcogenides, NaInS\(_{2-x}\)Se\(_x\) (x = 0, 0.5, 1.0, 1.5 and 2.0) solid solutions \[10\]. In 2020, Yaseen et al. \[11\] have reported interesting results on electronic, optical and thermoelectric properties of predicted body centered tetragonal (BCT) chalcopyrite of NaInY\(_2\) (Y = S, Se, Te) with space group I-42d. This report shows that the NaInY\(_2\) (Y = S, Se, Te) compounds are promising materials for photovoltaic (infrared and visible region) and thermoelectric device applications. This indicates that such study of hexagonal chalcogenide semiconductor NaInX\(_2\) (X = S, Se) with space group R-3m should be of significant scientific interest. Until now, most of the experimental and theoretical studies on NaInX\(_2\) (X = S, Se) are concerned mainly with the structural and electronic properties of the compounds. But studies on electron localization function (ELF), charge density distribution and Mulliken charge population analysis are still unexplored.

Optical parameters also remained largely unexplored. The electronic structure of solids can further be understood using the knowledge of energy dependent optical properties \[12\]. The knowledge of absorption coefficient, refractive indices and dielectric functions are essential to design optoelectronic devices. In addition to possible photovoltaic/optoelectronic applications of these compounds, the tunable bandgap and layered crystal structure further indicate the possible use as potential thermoelectric materials.

The coefficient of thermoelectric performance is conventionally measured by the dimensionless figure of merit defined as \(ZT = \frac{S^2\sigma T}{\kappa}\), where \(S\), \(\sigma\), \(\kappa\) (\(= \kappa_e + \kappa_i\)) and \(T\) stand for Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively \[13–15\]. In general, layered materials exhibit comparatively low thermal conductivity which is essential for achieving high \(ZT\) value \[15\]. To the best of our knowledge, no experimental or theoretical data on optical (except
absorption spectra [3]) and thermoelectric properties are available in literature. Therefore, a first-principles study will be performed to investigate electronic, optical and thermoelectric transport properties of hexagonal NaInX₂ (X = S, Se) in order to fill this significant research gap and to check the feasibility of their applications in optoelectronic and thermoelectric device sectors.

2 Computational methodology

The crystal structures of layered NaInX₂ (X = S, Se) compounds have been optimized using CASTEP code [16, 17] which is based on the density functional theory (DFT) [18, 19]. The plane wave basis set cut-off is set to 500 eV, and for the sampling of the Brillouin zone, a 15 × 15 × 23 Monkhorst–Pack mesh is employed [20]. The ground state energy of the system can be obtained by the solution of the Kohn–Sham equation in order to evaluate the electron exchange-correlations energy within the generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof (PBE) [19, 21]. In CASTEP code, the geometry optimization of a system can be obtained using two methods: Broyden Fletcher Goldfarb Shanno (BFGS) and damped molecular dynamics. Here, we have applied the BFGS method to optimize the atomic site configuration [22]. The geometry optimization is achieved using convergence thresholds of 5 × 10⁻⁶ eV/atom for the total energy, 0.01 eV/Å for the maximum force, 0.02 GPa for the maximum stress and 5 × 10⁻⁴ Å for maximum atomic displacement. The optimized crystal structures have been used for all calculations in the present study. The electronic band structures were calculated in WIEN2k [23] using the GGA within the PBE [19, 21] scheme and the Tran-Blaha modified Becke-Johnson potential (TB-mBJ) [24]. To obtain a good convergence of the basis set, a plane wave cut off of kinetic energy RKₘₐₓ = 7.0 was selected. A dense mesh of (31 × 31 × 5) k-points was used in the electronic, optical and transport properties calculations. The TB-mBJ potential was used for optical and thermoelectric transport properties calculations. The transport properties were calculated by solving semiclassical Boltzmann transport equations as implemented in the widely used BoltzTraP code [25]. The equation for the transport coefficients are defined in the Boltzmann transport theory [26, 27] based on the relaxation time approach.

3 Results and discussion

3.1 Structural properties

The chalcogenide compounds, NaInS₂ and its counterpart NaInSe₂ belong to the hexagonal crystal structure with space group R-3m (No. 166) [1, 2]. Figure 1 shows the two- and three-dimensional crystal structure of the NaInS₂ compound. The constructed unit cell has three formula units that contain a total of twelve atoms. The crystallographic lattice parameters and atomic positions as well as the percentage of deviation from earlier reports are tabulated in Table 1 along with available experimental and theoretical results. A maximum discrepancy of the present calculation is found to be 1.70% for the lattice constant a. This deviation of lattice constant from experimental value seems to be fair as the accuracy in theoretical calculations usually depends on the choice of the pseudopotential.

3.2 Electronic properties, Mulliken atomic population, charge density and electron localization function

The previous theoretical study on electronic properties was not adequate in view of the available
Table 1 The crystallographic lattice constants and Wyckoff atomic positions of NaInS$_2$ and NaInSe$_2$ compounds

| Phases     | $a$ (Å) | % of deviation | $c$ (Å) | % of deviation | Remarks | Atomic positions |
|------------|---------|----------------|---------|----------------|---------|------------------|
| NaInS$_2$  | 3.868   | 1.70           |         |                | This    | Na 0.0 0.0 0.5   |
|            | 3.803   |                | 20.134  | 1.22           | Expt. [3]| In 0.0 0.0 0.0   |
| NaInSe$_2$ | 4.022   | 1.25           |         |                | This    | S/Se 0.0 0.0 0.26|
|            | 3.972   |                | 21.005  | 0.55           | Expt. [3]|                  |

Experimental results [3]. Owing to increased interest on prospective materials it is thus necessary to add more information and analyze on electronic properties which may help to design optoelectronic and thermoelectric device applications as well. Since the optical and transport properties strongly depend on electronic band structure of materials, the underestimated band gaps are not suitable to predict optical and transport parameters. A lot of prior studies have reported that GGA-PBE approach underestimate the band gap of semiconducting material while TB-mBJ potential produces band gaps in good agreement with the experimental results [13, 28–31].

In the electronic band structure, the Fermi level ($E_F$) is placed at 0 eV, and a distinct band gap between conduction and valence bands was found. The $E_F$ is located very close to the peak in the valence band. The valence band maximum (VBM) is found at the $\Gamma$ point for both NaInS$_2$ and NaInSe$_2$, while the conduction band minimum (CBM) is present at the $\Gamma$ point and $\Gamma$ point for NaInS$_2$ and NaInSe$_2$ compounds, respectively.

This implies that the NaInS$_2$ compound is an indirect band gap semiconductor and NaInSe$_2$ possesses a direct bandgap. Table 2 displays the band gaps obtained experimentally as well as theoretically using different pseudopotential approaches. The TB-mBJ estimated bandgaps are $\sim$ 3.3 and $\sim$ 2.3 eV for the NaInS$_2$ and NaInSe$_2$ compounds, respectively. These results are very much consistent with the experimental results [1, 3]. The lowest part of the conduction band is shifted significantly to lower energy at $\Gamma$ point while the upper part of the valence band was not noticeably shifted when the S is replaced by Se. This should be the reason for the reduced band gap for the NaInSe$_2$ compound. The total and partial DOS are studied here for the purpose of explaining the contribution from different atomic orbitals to the atomic bonding; charge transport and optical transitions as shown in Fig. 2b and d. The top of the valence band for both the compounds is mainly comprised of Na-2p, S-3s, S/Se-p (S for NaInS$_2$ and Se for NaInSe$_2$ compounds), and In-5p and In-4d electronic states. The lower part of valence bands around $\sim$ 4 eV originates from $s$ orbital of Na, In, and S/Se elements.

On the other hand, the bottom of the conduction bands above the $E_F$ is due to the hybridization among $s$ orbital of Na, In and S/Se states. Thus the band containing the CBM has the antibonding character between S/Se-$s$ and In-$p$ orbitals in both the compounds. This feature is more pronounced in the case of NaInS$_2$ than in NaInSe$_2$ compound [32]. The low energy part of the conduction band, therefore, resides at much higher energy ($\sim$ 3 eV) for NaInS$_2$ than ($\sim$ 2 eV) for NaInSe$_2$ compound as shown in Fig. 2c and d. This feature is mainly responsible for the reduced bandgap of the NaInSe$_2$. However, the top part of the valence bands is flatter than the conduction bands for both compounds. The flat nature of these bands comes from the strong hybridization of Na-2p, S-3s, S/Se-p, In-5p and In-4d orbitals which can also be clearly seen from the projected density of states shown in Fig. 2b and d. From Fig. 2b and d, it is clearly seen that the charge carriers in the In-d orbital have energies very close to the Fermi level. This suggests that the electrons in In-d orbitals will play a dominant role in electrical conduction under the influence of external stimuli.

The Mulliken atomic population (MAP) analysis and the charge density mapping (CDM) are also carried out with the help of the CASTEP code [16] to
gain knowledge on charge transfer mechanism as well as bonding between different atomic species and their nature [33]. The difference between the formal ionic charge and the Mulliken charge on the anion species in the material results in the effective valence charge (EVC). It is seen from the Table 3 that in both compounds, the charge of S/Se is negative; therefore, these elements should accept electron from other species in the material. Here, the MAP analysis revealed that in compound NaInS$_2$, the species In and/or Na donate 0.64 $|e|$ charge to S while those species transfer 0.33 $|e|$ charge to Se in the NaInSe$_2$ compound [12]. Therefore, the chemical bond could be formed only between Na-S/Se and In-S/Se due to the negative charge on S/Se. It is also fair to note that the bond between In-S/Se could be more covalent.
than Na-S/Se bond as the higher value of EVC signifies the higher level of covalency.

The CDM has also been studied to know the electron densities involved in the chemical bonds between the different atomic species. Figure 3a and b display the CDM for NaInS_2 and NaInSe_2 compounds. The CDM produces a density difference field which usually displays the changes in the electron distribution in the materials system [34]. As observed in Fig. 3, strong covalent bonding can be attributed between In and S atoms whereas comparatively weaker covalent bond is found between Na and S atom for the NaInS_2 compound. Similar bonding character could also be observed in the case of NaInSe_2 compound. These phenomena are consistent with the MAP analysis.

Electron localization function (ELF) is also studied to get a better understanding of the type of bonding in the studied ternary chalcogenides. It is seen from the results of ELF (as shown in Fig. 4) that a strong accumulation of electrons around S/Se is found in both compounds. This indicates that the element S/Se receives charge from neighboring In and/or Na atomic species. Thus, strong bondings between Na/In-S/Se atomic species are realized. The results of ELF are consistent with the results of CDM and Mulliken population analysis.

It is known that thermoelectric properties of materials are directly related to their electronic structure. The favorable band gap of the titled compounds has encouraged us to perform calculations regarding thermoelectric properties, which is described in the next section.

### 3.3 Thermoelectric transport properties

Since the study of electronic properties confirms the semiconducting nature of the NaInX_2 (X = S, Se), it is interesting to study their thermoelectric properties. A potential thermoelectric material should have low thermal conductivity (κ) and high power factor (S^2σ). The high power factor simply depends on the high Seebeck coefficient and electrical conductivity. A suitable combination of these two parameters ensures a high thermoelectric figure of merit (ZT) [35], which is a challenging task to achieve. The temperature-dependent thermoelectric transport properties such as Seebeck coefficient (S), the ratio between electrical conductivity and the relaxation time (σ/τ), power factor (S^2σ/τ) and thermal conductivity (κ_total) have been calculated using TB-mBJ potential along two crystallographic directions, a and c in the temperature range from 300 to 1000 K. The phonon contribution to the thermal conductivity of the compounds of interest was calculated in a recent study [10]. All these transport coefficients are plotted for the NaInX_2 (X = S, Se) compounds in Fig. 5a–h. The anisotropy in the electronic band structure leads to the anisotropic features in the transport coefficients. Anisotropic thermoelectric materials with some specific features have excellent applications in modern thin film technology. Many anisotropic thermoelectric

| Compound | Mulliken atomic population |
|----------|-----------------------------|
| Atoms    | S   | p   | D   | Total | Charge (e) | EVC (e) |
| NaInS_2  | Na  | 2.18| 6.22| –     | 8.39      | 0.61    | 0.39   |
|          | In  | 1.01| 1.32| 10.00| 12.33     | 0.67    | 2.33   |
|          | S   | 1.87| 4.77| –     | 6.64      | –       | –      |
| NaInSe_2 | Na  | 2.22| 6.38| –     | 8.60      | 0.40    | 0.60   |
|          | In  | 1.33| 1.42| 10.00| 12.75     | 0.25    | 2.75   |
|          | Se  | 1.65| 4.67| –     | 6.33      | –       | –      |
devices such as micro-sensors of radiation, heat-flux sensors and laser-radiation detectors are the important fields of applications for thermoelectric materials with anisotropic behavior. Direction dependent properties add to the available degrees of freedom in device applications [36]. The Seebeck coefficient $S$ measures the potential difference in different semiconductors or metals induced between two junctions when a temperature gradient is established. The magnitude of this parameter depends critically on the energy derivative of the logarithmic of the electrical conductivity. Therefore, a very close link with the underlying electronic band structure is a natural consequence. It should be noted here that to calculate the different thermoelectric parameters, a fixed relaxation time $\tau = 10^{-14}$ s has been used in calculations as for most of the semiconducting materials this is in the range of $10^{-14}$ s–$10^{-15}$ s [37, 38]. It is explicit from Fig. 5a and e that a gradual increasing trend of $S$ along $c$ direction is observed with temperature up to 800 K and then it reaches a constant value of 295 $\mu$V/K and 300 $\mu$V/K for NaInS$_2$ and NaInSe$_2$, respectively. This implies that thermally generated electron–hole pairs contribute positively to $S$ along the $c$ direction. On the other hand, the value of $S$ along $a$ direction is gradually decreased with temperature. The positive value of $S$ attests the domination of $p$-type conduction in both NaInS$_2$ and NaInSe$_2$.

The very low value of $\sigma/\tau$ at low temperatures represents the near insulating behavior of these compounds (very few of the electrons in the valence band are transferred to the conduction band for charge transport). It is seen from Fig. 5b and f that $\sigma/\tau$ increases rapidly with increasing temperature and this behavior indicates the semiconducting nature of NaInS$_2$ and NaInSe$_2$ compounds. The estimated value of $\sigma/\tau$ at room temperature (300 K) is found to be $10.74 \times 10^{18}$ ($\Omega$ms)$^{-1}$ and $9.93 \times 10^{18}$ ($\Omega$ms)$^{-1}$ along $a$ direction and $0.8065 \times 10^{18}$ ($\Omega$ms)$^{-1}$ and $0.7442 \times 10^{18}$ ($\Omega$ms)$^{-1}$ along $c$ direction for the NaInS$_2$ and NaInSe$_2$ compounds, respectively.

These results clearly suggest that the $\sigma/\tau$ along $a$ direction is much higher than that along $c$ direction. The power factors ($S^2\sigma/\tau$) for both compounds also follow the same trend of $S$ and $\sigma/\tau$ as depicted in Fig. 5c and g. The maximum estimated values of $S^2\sigma/\tau$ (with $\tau = 10^{-14}$ s) for the NaInS$_2$ at 1000 K are 151.49 $\mu$W/cmK$^2$ and 52.77 $\mu$W/cmK$^2$ whereas those for the NaInSe$_2$ are 154.34 $\mu$W/cmK$^2$ and 44.58 $\mu$W/
cmK$^2$ along $a$ and $c$ directions, respectively. These values for both compounds along $a$ direction are much higher (∼15 times) than that of 10.1 μW/cmK$^2$ along $b$-axis at 850 K for the state-of-the-art thermoelectric material, SnSe [15]. The thermal conductivity, $\kappa_{\text{total}}$ is a combination of electronic thermal conductivity ($\kappa_e$) and lattice thermal conductivity ($\kappa_l$) where the $\kappa_l$ measures the heat conduction due to the vibration of the lattice ions in a material. The details calculation of $\kappa_l$ for these studied compounds can be found in the literature [10]. The values of $\kappa_{\text{total}}$ for the NaInS$_2$ and NaInSe$_2$ at 1000 K are almost the same which are ∼ 21.9073 W/mK and ∼ 7.7156 W/mK along $a$ and $c$ crystallographic axes, respectively.

We have also found that at low temperatures (less than 300 K), the $\kappa_l$ is dominating but at a higher temperature (above 300 K) $\kappa_e$ starts to dominate. It is readily seen from the Fig. 5 that all thermoelectric parameters for the NaInS$_2$ and NaInSe$_2$ compounds are significantly anisotropic. All parameter values except $S$ along crystallographic $a$ direction are significantly higher along $a$ than in $c$ direction. The efficiency of thermoelectric materials can be gauged using the dimensionless figure of merit, $ZT = \frac{S^2 \sigma}{\kappa T}$. The calculated $ZT$ values along two crystallographic axes for both the compounds are presented in Fig. 6a and b. It is found that $ZT$ values increase with temperature and there is a strong anisotropy upto 800 K.
and after that both compounds exhibit less anisotropy. The $ZT$ values along $a$-axis for both the compounds at 1000 K are almost the same and it is estimated to be $\sim 0.7$. This $ZT$ value is higher than that for recently reported body centered tetragonal (BCT) chalcopyrite material NaInSe$_2$ [11].

We have also studied the variations of $S$, $\sigma/\tau$, $\kappa_e/\tau$ and $S^2\sigma/\tau$ with carrier concentration at different temperatures for both the materials as depicted in Fig. 7a–h. In all figures, the green, red, and blue colors represent the TE parameters at temperatures 600, 900 and 1200 K, respectively. The solid and dashed lines represent TE parameters along $a$- and $c$-axes, respectively. It is obvious from Fig. 7a and e for both compounds that as the temperature increases $S$ decreases and this behavior can be explained precisely using the equation for $S$ for bulk semiconducting material, $S = \frac{8e^2\sqrt{T}}{3\hbar^2m^*}m^*(\frac{e}{m^*})^{2/3}$ [39]. It is seen that $S$ largely depends on carrier concentration, carrier effective mass and temperature. $S$ decreases with the increasing carrier concentration $n$ because $S$ is inversely related to $n$. For semiconducting materials it is usual that carrier concentration increases with temperature. It is also clear from Fig. 7b, d, f and h that a gradually increasing trend of $\sigma/\tau$ and $\kappa_e/\tau$ for both compounds is observed as a function of carrier concentration as they follow the fundamental equations $\sigma = ne\mu$ and $\kappa_e = L\alpha T$, respectively. The power factor is determined by the combined effect of Seebeck coefficient and electrical conductivity, expressed as $(S^2\sigma/\tau)$. The maximum power factors for both compounds are found to be increased with temperature at around $2 \times 10^{21}$ cm$^{-3}$ as depicted in Fig. 7c and g.

We have summarized the data at temperatures 300 K and 1000 K for different thermoelectric parameters for the NaInS$_2$ and NaInSe$_2$ compounds in Table 4. The obtained $ZT$ values are not suitable for direct practical applications and the high value of $\kappa$ is mainly responsible for this low value of $ZT$. The reduction of thermal conductivity is very important to achieve significantly higher $ZT$ value for practical applications in thermoelectric devices. A strategy (e.g., by nano-structuring [40] and all-scale hierarchical architecture [41]) to reduce lattice thermal conductivity, $k_l$ might significantly increase the efficiency of these prospective thermoelectric materials. The reduction of band gap of both compounds through band engineering will also be interesting and can lead to the enhancement of thermoelectric performance. However, all the other studied thermoelectric parameters, especially high power factor and figure of merit, clearly indicate that both NaIn$X_2$ ($X = S, Se$) compounds have potentials to be used for thermoelectric device applications.

### 3.4 Optical properties

The optical properties of solids are measurable macroscopic physical properties which can be studied by the calculations of the energy dependent dielectric function (directly related to the electronic band structure). The dielectric function (real and imaginary parts) elucidates the various optical properties of solids completely [42]. The study of these properties is also desirable to predict the suitability of solids for possible applications. Therefore, the dielectric function $\varepsilon(\omega)$ is calculated and used to study the optical properties of the NaInS$_2$ and NaInSe$_2$ compounds. It is well-known that the imaginary part of the dielectric function, $\varepsilon_2(\omega)$ is a precondition to estimate the rest of the optical constants such as the real part of the dielectric function and the optical conductivity.
Fig. 7  Carrier concentration
dependence of a Seebeck
coefficient (S), b electrical
conductivity over relaxation
time (σ/τ), c power factor
(S^2σ/τ) and d electronic
thermal conductivity (k_e) along
a and c directions for NaInS$_2$
compounds at temperature at
temperatures 600, 900 and
1200 K. e–h same parameters
for NaInSe$_2$

Table 4  Seebeck coefficient (S), electrical conductivity (σ), power factor (S^2σ) and thermal conductivity (κ$_{\text{total}}$) (with τ = 10$^{-14}$ s) along ‘a’ and ‘c’ directions for NaInX$_2$ (X = S, Se) crystals

| Compound   | Temperature (K) | S (µV/K)   | σ $\times 10^4$ (Ωm)$^{-1}$ | (S^2σ)$_{\text{max}}$ (µW/cmK²) | κ$_{\text{total}}$ (W/mK) |
|------------|----------------|------------|-------------------------------|--------------------------------|--------------------------|
| NaInS$_2$  | 300            | 226.12[a]  | 10.74 [a]                     | 54.90 [a]                      | 6.49 [a]                 |
|            | 1000           | 00.00 [a]  | 38.91 [a]                     | 151.49 [a]                     | 21.91 [a]                |
| NaInSe$_2$ | 300            | 227.92[a]  | 9.93 [a]                      | 51.56 [a]                      | 05.63 [a]                |
|            | 1000           | 00.00 [a]  | 37.66 [a]                     | 154.34 [a]                     | 22.07 [a]                |
function $\varepsilon_1(\omega)$, refractive index, absorption spectrum, loss-function, reflectivity and optical conductivity of the material. One obtains $\varepsilon_1(\omega)$ from the calculated spectrum of $\varepsilon_2(\omega)$ via the Kramers–Kronig transformation relation [43]. All other optical constants can be extracted from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. The detail method and related formulae for these optical constants using a full-potential augmented plane wave method (FPLAPW) as implemented in WIEN2k can be found in the literature [43, 44].

Here, we have studied the optical properties for two polarization directions [100] and [001] and found that the shape of the curves for these polarizations are almost identical but energy positions of various peaks are clearly different and distinguishable. Noted here that the positions of the peak for different optical parameters are gradually shifted to the higher energy region when light is incident onto the materials with [001] polarization as shown in Figs. 8 and 9. Optical anisotropy is related to the anisotropic optical response depending on the state of polarization of the incident electromagnetic field. Optical anisotropy is helpful for fabrication of display devices such as LCD screens, screens for 3D movies etc.

Figure 8a and e display the obtained spectra for the imaginary part of the dielectric function which arises simply from direct interband transitions while indirect band transitions are ignored because of their minor contribution due to phonon scattering contribution to the dielectric function [45]. The real part of the dielectric function is also presented in Fig. 8b and f. The imaginary part of the dielectric function is related to the absorption spectra of the compounds while the real part is related to the polarizability of the materials [45]. From the onset of optical absorption, the obtained bandgap values are $\sim 3.3$ and $\sim 2.3$ eV for NaInS$_2$ and NaInSe$_2$, respectively, which agree very well with those obtained from electronic band structure calculations. Figure 8a and e also demonstrate that the absorption spectrum for NaInSe$_2$ starts at lower energy than that for NaInS$_2$. The difference in the spectra of $\varepsilon_2(\omega)$ for NaInS$_2$ and NaInSe$_2$ is also due to the difference in the bandgap values which decrease when S is replaced by Se. The three consecutive sharp peaks at around 5.0, 6.4, 8.0 and 4.2, 5.6, 7.0 (all in eV) for [100] polarization whereas those at around 5.0, 6.6, 7.8 and 4.4, 6.0, 6.9 (all in eV) for [001] polarization for NaInS$_2$ and NaInSe$_2$, respectively, occur due to the interband transitions from S-$s/p$ and Se-$s/p$ states to the In-$s$ states at the bottom of the conduction bands.

The real part of dielectric constant $\varepsilon_1(\omega)$ at zero frequency is known as the static dielectric constant $\varepsilon_1(0)$. The calculated values of the real part of the

![Fig. 8](image-url)
static dielectric function, $\varepsilon_1(0)$, static refractive index, $n(0)$, absorption band edge (ABE(0)) and reflectivity ($R$) along [100] and [001] polarization directions for NaInS$_2$ and NaInSe$_2$ compounds at zero photon energy are summarized in Table 5. The values of $\varepsilon_1(0)$ are $4.85$ and $6.06$ for [100] polarization and $4.40$ and $5.38$ for [001] polarization for NaInS$_2$ and NaInSe$_2$, respectively. These values are in good accord with the Penn model [46] expressed as,

$$\varepsilon_1(0) = 1 + \left(\frac{\hbar \omega_p}{E_g}\right)^2.$$ 

It means that solids with high values of $\varepsilon_1(0)$ have lower energy band gaps for a fixed plasma frequency. The real part of the refractive index, $n(\omega)$ measures the phase velocity whereas the amount of absorption loss is usually measured by the imaginary part (extinction coefficient) when light (photon) penetrates into the material. The obtained $n(\omega)$ of NaInS$_2$ and NaInSe$_2$ are shown in Fig. 8c and g where the static refractive index $n(0)$ have the values of ranging 2.1–2.20 and 2.32–2.46 for NaInS$_2$ and NaInSe$_2$, respectively. The value of the refractive index is lower for the semiconductors that have higher bandgap energy. The maximum refractive index (MRI) for NaInS$_2$ and NaInSe$_2$ is obtained at energy of 3.30 eV for [100] polarization and at 3.50 eV for [001] polarization, respectively. The MRI occurs at the corresponding incident energy where the transitions of electrons from the valence band to conduction band occur and the transitions is referred to as direct electron transition. Figure 8d and h show the variation of the extinction coefficient with photon energy. The extinction coefficient increases with energy and the maximum values are attained at around 8.50 eV and 7.80 eV for [001] polarization for NaInS$_2$ and NaInSe$_2$ compounds, respectively. It is also observed that the variation of $n(\omega)$ and $k(\omega)$ largely follow the variation of $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$.

| Compound     | $\varepsilon_1(0)$ [100] | $\varepsilon_1(0)$ [001] | $n(0)$ [100] | $n(0)$ [001] | ABE (0) [100] (eV) | ABE(0) [001] (eV) | $R(0) \times 100\%$ [100] | $R(0) \times 100\%$ [001] |
|--------------|--------------------------|--------------------------|--------------|--------------|------------------|------------------|------------------------|------------------------|
| NaInS$_2$    | 4.85                     | 4.41                     | 2.20         | 2.10         | 3.01             | 3.20             | 14.10                  | 12.59                  |
| NaInSe$_2$   | 6.06                     | 5.38                     | 2.46         | 2.32         | 2.25             | 2.46             | 17.82                  | 15.80                  |
respectively, with incident photon energy. It is noteworthy that the values of $\varepsilon_1(0)$ and $n(0)$ of both the compounds under study reveal higher values than those for the tetragonal chalcopyrite NaInS$_2$ and NaInSe$_2$ compounds [11]. It is known that high values of $\varepsilon_1(0)$ and $n(0)$ are useful in optoelectronic device fabrications including LCDs, OLEDs, and quantum dot (QDLED) display.

Figure 9a and e exhibit the optical absorption coefficients that provide information about loss of energy of penetrating light through the solids and prerequisite knowledge to design optoelectronic devices. The spectra started to rise (also known as absorption edge) after a finite value of incident energy approximately equal to the energy band gap values for both compounds owing to their semiconducting nature. It is also noticeable that the spectrum for NaInSe$_2$ starts at lower energy than NaInS$_2$ because of its lower band gap as shown in Table 5. The spectra are observed to increase with some prominent peak with the variation of photon energy. The strongest absorption region is from 3.0 to 11.0 eV for NaInS$_2$ and from 2.5 to 12 eV for NaInSe$_2$. The highest broad absorption peak in the ultraviolet (UV) region makes NaInS$_2$ and NaInSe$_2$ potential candidates for use in the area of transparent coatings in the visible and deep UV regions [31]. The reflectivity spectra falls sharply from a high value [49]. The highest sharp peak in the loss function is observed at around 13 eV due to bulk plasmonic excitation for both the compounds, which corresponds to the sudden decline of reflectivity. The energy at this point (maximum of $L(\omega)$) is termed as plasmon energy and the corresponding frequency is called plasma frequency, $\omega_p$. The plasmon energy as well as plasma frequency, $\omega_p$, can also be correlated with the $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ of the dielectric functions where both the spectra for [001] polarization have the tendency to go through zero while those for the[100] polarization do not follow the same trend. These features are seen in Figs. 8a, b, e and f, and 9d and h. Finally, the tunable electronic band gap, high dielectric constant, good absorption spectra and high photoconductivity clearly indicate that both the ternary layered chalcogenide materials (NaInS$_2$ and NaInSe$_2$) can be used in optoelectronic applications.

### 4 Conclusions

To summarize, we have computed the structural and unexplored electronic (density of state, Mulliken atomic population and charge density), optical and thermoelectric transport properties of NaInS$_2$ and NaInSe$_2$ using the first principles method. Our calculated lattice parameters are consistent with the experimentally found results. A distinct band gap between valence and conduction band is observed. The analysis of the Mulliken bond population and charge density mapping shows that the bond between In-S/Se should be more covalent than the Na-S/Se bond. Optical and thermoelectric properties are anisotropic. Carrier concentration dependent thermoelectric properties at 900 K such as Seebeck coefficient ($S$), electrical conductivity ($\sigma$), power factor ($S^2\sigma$) and electronic thermal conductivity ($k_e$) have been calculated and discussed. The highest values of $S$ (in $\mu$V/K) of 295 and 300 at temperature 1000 K along a direction are realized for NaInS$_2$ and NaInSe$_2$ compounds, respectively. The positive value of $S$ attests the dominance of $p$-type conduction channel. The electrical conductivity ($\sigma$) at 300 K is estimated to be $10.74 \times 10^4$ ($\Omega$m)$^{-1}$ and $9.93 \times 10^4$ ($\Omega$m)$^{-1}$ along $a$ direction and $0.8065 \times 10^4$ ($\Omega$m)$^{-1}$ and $0.7442 \times 10^4$ ($\Omega$m)$^{-1}$ along $c$ direction for NaInS$_2$ and NaInSe$_2$ compounds, respectively. This shows that the $\sigma$ along $a$ direction is much higher than that
along c direction. The power factor ($S^2\sigma$) exceeds 151.34 $\mu$W/cmK$^2$ for both compounds along a direction which is much higher than that of the state-of-the-art thermoelectric material, SnSe of 10.1 $\mu$W/cmK$^2$. The obtained ZT value of $\sim$ 0.7 is higher than that of the tetragonal chalcopryte of NaInSe$_2$. The ZT value can be further increased via band gap engineering. Another approach could be insertion of suitable atomic layers in NaInS$_2$ and NaInSe$_2$ to reduce the thermal conductivity without affecting the electrical conductivity. Such intercalation is relatively easy for materials which have layered structure to begin with. The absorption coefficient and photoconductivity spectra confirm the semiconducting nature of these materials, which are consistent with calculated electronic band structure and previous reports. The sharp absorption peak in the ultraviolet region indicates the possible use of these materials for fabricating devices to stabilize surgical equipments. Based on impressive optical and thermoelectric properties, it can be concluded that the ternary layered chalcogenides NaInS$_2$ and NaInSe$_2$ could be suitable candidates for thermoelectric and optoelectronic device applications. Experimental verifications of the results presented herein are expected and we hope that this study will serve as a reference for future experimental and theoretical studies on these interesting systems which hold significant prospect in energy harvesting and optical device applications.

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**Data availability**

The datasets generated during the current study are available from the corresponding author on a reasonable request.

**Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**References**

1. K. Fukuzaki, S. Kohiki, S. Matsushima, M. Oku, T. Hide-shima, T. Watanabe, S. Takahashi, H. Shimooka, Preparation and characterization of NaInO$_2$ and NaInS$_2$. J. Mater. Chem. 10, 779–782 (2000). https://doi.org/10.1039/A90850J
2. R. Hoppe, W. Lidecke, F.-C. Frorath, Zur Kenntnis von NaInS$_2$ und NaInSe$_2$. Zeitschrift für organische und allgemeine Chemie. 309, 49–54 (1961). https://doi.org/10.1002/zaac.196103090105
3. N. Takahashi, H. Ito, A. Miura, N.C. Rosero-Navarro, Y. Goto, Y. Mizuguchi, C. Moriyoshi, Y. Kuroiwa, M. Nagao, S. Watauchi, I. Tanaka, K. Tadanaga, Synthesis, crystal structure and optical absorption of NaInS$_{2-x}$Se$_x$. J. Alloys Compd. 750, 409–413 (2018). https://doi.org/10.1016/j.jallcom.2018.03.407
4. S. Wagner, J.L. Shay, P. Migliorato, H.M. Kasper, CuInSe$_2$/CdS heterojunction photovoltaic detectors. Appl. Phys. Lett. 25, 434–435 (1974). https://doi.org/10.1063/1.1655537
5. A. Kudo, A. Nagane, I. Tsuji, H. Kato, H$_2$ Evolution from aqueous potassium sulfite solutions under visible light irradiation over a novel sulfide photocatalyst nains$_2$ with a layered structure. Chem. Lett. 31, 882–883 (2002). https://doi.org/10.1246/cl.2002.882
6. P. Hu, C.K. Ngaw, Y.Y. Tay, S. Cao, J. Barber, T.T.Y. Tan, S.C.J. Loo, A “uniform” heterogeneous photocatalyst: integrated p–n type CuInS$_2$/NaInS$_2$ nanosheets by partial ion exchange reaction for efficient H$_2$ evolution. Chem. Commun. 51, 9381–9384 (2015). https://doi.org/10.1039/C5CC02237A
7. Z. Mei, S. Ouyang, D.-M. Tang, T. Kako, D. Golberg, J. Ye, An ion-exchange route for the synthesis of hierarchical In$_2$S$_3$/ZnIn$_2$S$_4$ bulk composite and its photocatalytic activity under visible-light irradiation. Dalton Trans. 42, 2687–2690 (2013). https://doi.org/10.1039/C2DT32721D
8. A. Miura, T. Oshima, K. Maeda, Y. Mizuguchi, C. Moriyoshi, Y. Kuroiwa, Y. Meng, X.-D. Wen, M. Nagao, M. Higuchi, K. Tadanaga, Synthesis, structure and photocatalytic activity of layered LaOInS$_2$. J. Mater. Chem. A 5, 14270–14277 (2017). https://doi.org/10.1039/C7TA04440B
9. R. Saniz, J. Bekaert, B. Partoens, D. Lamoen, Structural and electronic properties of defects at grain boundaries in CuInSe$_2$. Phys. Chem. Chem. Phys. 19, 14770–14780 (2017). https://doi.org/10.1039/C7CP02033C
10. M.M. Hossain, M.A. Ali, M.M. Uddin, M.A. Hossain, M. Rasadujaman, S.H. Naqib, M. Nagao, S. Watauchi, I. Tanaka, Influence of Se doping in recently synthesized NaInS$_{2-x}$Se$_x$ solid solutions for potential thermo-mechanical applications studied via first-principles method [Cond-Mat]. (2020). http://arxiv.org/abs/2010.01796. Accessed 9 Oct 2020.
11. M.S. Yaseen, G. Murtaza, G. Murtaza, Theoretical investigation of the structural stabilities, optoelectronic and thermoelectric properties of ternary alloys NaInY$_2$ (Y = S, Se and Te) through modified Becke-Johnson exchange potential. Int. J. Mod. Phys. B. 34, 2050133 (2020). https://doi.org/10.1142/S0217979220501337

12. P. Barua, M.M. Hossain, M.A. Ali, M.M. Uddin, S.H. Naqib, A.K.M.A. Islam, Effects of transition metals on physical properties of M$_2$BC (M = V, Nb, Mo and Ta): a DFT calculation. J. Alloys Compd. 770, 523–534 (2019). https://doi.org/10.1016/j.jallcom.2018.08.155

13. E. Haque, M.A. Hossain, First-principles study of elastic, electronic, thermodynamic, and thermoelectric transport properties of TaCoSn. Results Phys. 10, 485–486 (2018). https://doi.org/10.1016/j.rinp.2018.06.053

14. E. Haque, M.A. Hossain, First-principles study of mechanical, thermodynamic, transport and superconducting properties of Sr$_5$SnO$_3$. J. Alloys Compd. 730, 279–283 (2018). https://doi.org/10.1016/j.jallcom.2017.09.299

15. L.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V.P. Dravid, M.G. Kanatzidis, Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals. Nature 508, 373–377 (2014). https://doi.org/10.1038/nature13184

16. M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, First-principles simulation: ideas, illustrations and the CASTEP code. J. Phys. 14, 2717–2744 (2002). https://doi.org/10.1088/0953-8984/14/11/301

17. S.J. Clark, M.D. Segall, C.J. Pickard, P.J. Hasnip, M.J.J. Probert, K. Refson, M.C. Payne, First principles methods using CASTEP. ZeitschriftFürKristallographie - Crystalline Materials. 220, 567–570 (2005). https://doi.org/10.1524/zkri.220.5.567.6075

18. P. Hohenberg, W. Kohn, Inhomogeneous electron gas. Phys. Rev. 136, B864–B871 (1964). https://doi.org/10.1103/PhysRev.136.B864

19. J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996). https://doi.org/10.1103/PhysRevLett.77.3865

20. H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations. Phys. Rev. B 13, 5188–5192 (1976). https://doi.org/10.1103/PhysRevB.13.5188

21. W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects. Phys. Rev. 140, A1133–A1138 (1965). https://doi.org/10.1103/PhysRev.140.A1133

22. T.H. Fischer, J. Almlof, General methods for geometry and wave function optimization. J. Phys. Chem. 96, 9768–9774 (1992). https://doi.org/10.1021/j100203a036

23. P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, R. Laskowsk, F. Tran, L. Marks, L. Marks, WIEN2k: An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties. Techn. Universität, 2019. https://www.scholars.northwestern.edu/en/publications/wien2k-an-augmented-plane-wave-plus-local-orbitals-program-for-ca. Accessed 23 Sept 2020

24. F. Tran, P. Blaha, Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential. Phys. Rev. Lett. 102, 226401 (2009). https://doi.org/10.1103/PhysRevLett.102.226401

25. G.K.H. Madsen, D.J. Singh, B. TraP, A code for calculating band-structure dependent quantities. Comput. Phys. Commun. 175, 67–71 (2006). https://doi.org/10.1016/j.cpc.2006.03.007

26. K. Parlinski, Z.Q. Li, Y. Kawazoe, First-principles determination of the soft mode in cubic ZrO$_2$. Phys. Rev. Lett. 78, 4063–4066 (1997). https://doi.org/10.1103/PhysRevLett.78.4063

27. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A.D. Corso, S.D. Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Scaccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, R.M. Wentzcovitch, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J. Phys. Condens. Matter. 21, 395502 (2009). https://doi.org/10.1088/0953-8984/21/39/395502

28. M. Irfan, S. Azam, S. Hussain, S.A. Khan, M. Sohail, M. Ahmad, S. Goumi-Said, Enhanced thermoelectric properties of ASbO$_3$ due to decreased band gap through modified beckejohnson potential scheme. J. Phys. Chem. Solids. 119, 85–93 (2018). https://doi.org/10.1016/j.jpcs.2018.03.010

29. E. Haque, M.A. Hossain, Origin of ultra-low lattice thermal conductivity in Cs$_3$BiAgX$_6$ (X=Cl, Br) and its impact on thermoelectric performance. J. Alloys Compd. 748, 63–72 (2018). https://doi.org/10.1016/j.jallcom.2018.03.137

30. S. Sharma, B. Singh, P. Kumar, A comparative study of thermoelectric properties of CuGaTe$_2$ by using PBE and MBJ potentials. AIP Conf. Proc. 1942, 140036 (2018). https://doi.org/10.1063/1.5029167

31. M.A. Ali, M. Anwar Hossain, M.A. Rayhan, M.M. Hossain, M.M. Uddin, M. Roknuzzaman, K. Ostrikov, A.K.M.A. Islam, S.H. Naqib, First-principles study of elastic, electronic, optical and thermoelectric properties of newly synthesized K$_2$Cu$_2$GeS$_4$chalcochendine. J. Alloys Compd. 781, 37–46 (2019). https://doi.org/10.1016/j.jallcom.2018.12.035

Springer
32. I.S. Khare, N.J. Szymanski, D. Gall, R.E. Irving, Electronic, optical, and thermoelectric properties of sodium pnictogen-chalcogenides: a first principles study. Comput. Mater. Sci. 183, 109818 (2020). https://doi.org/10.1016/j.commatsci.2020.109818

33. M. Roknuzzaman, M.A. Hadi, M.A. Ali, M.M. Hossain, N. Jahan, M.M. Uddin, J.A. Alarco, K. Ostrikov, First hafnium-based MAX phase in the 312 family, Hf₃AlC₂: a first-principles study. J. Alloys Compd. 727, 616–626 (2017). https://doi.org/10.1016/j.jallcom.2017.08.151

34. M.T. Nasir, M.A. Hadi, M.A. Rayhan, M.A. Ali, M.M. Hossain, M. Roknuzzaman, S.H. Naqib, A.K.M.A. Islam, M.M. Uddin, K. Ostrikov, First-principles study of superconducting ScRhP and ScIrP pnictides. Physica Status Solidi (B). 254, 1700336 (2017). https://doi.org/10.1002/pssb.201700336

35. J. He, T.M. Tritt, Advances in thermoelectric materials research: looking back and moving forward. Science (2017). https://doi.org/10.1126/science.aak9997

36. A.T. Burkov, A. Heinrich, M.V. Vedernikov, Anisotropic thermoelectric materials, properties and applications. AIP Conf. Proc. 316, 76–80 (1994). https://doi.org/10.1063/1.46838

37. C. Jacoboni, The Theory of Electron Transport in Semiconductors: A Pathway from Elementary Physics to Nonequilibrium Green Functions (Springer-Verlag, Berlin Heidelberg, 2010).

38. R.L. González-Romero, A. Antonelli, Estimating carrier relaxation times in the Ba₈Ga₁₆Ge₃₀ clathrate in the extrinsic regime. Phys. Chem. Chem. Phys. 19, 3010–3018 (2017). https://doi.org/10.1039/C6CP08026J

39. Z. Gao, G. Liu, J. Ren, High thermoelectric performance in two-dimensional tellurium: an Ab initio study. ACS Appl. Mater. Interfaces. 10, 40702–40709 (2018). https://doi.org/10.1021/acsami.8b11836

40. K.F. Hsu, S. Loo, F. Guo, W. Chen, J.S. Dyck, C. Uber, T. Hogan, E.K. Polychroniadi, M.G. Kanatzidis, Cubic AgPb₉SbTe₂₃: bulk thermoelectric materials with high figure of merit. Science 303, 818–821 (2004). https://doi.org/10.1126/science.1092963

41. K. Biswas, J. He, I.D. Blum, C.-I. Wu, T.P. Hogan, D.N. Seidman, V.P. Dravid, M.G. Kanatzidis, High-performance bulk thermoelectrics with all-scale hierarchical architectures. Nature 489, 414–418 (2012). https://doi.org/10.1038/nature11439

42. C.C. Kim, J.W. Garland, H. Abad, P.M. Raccah, Modeling the optical dielectric function of semiconductors: extension of the critical-point parabolic-band approximation. Phys. Rev. B 45, 11749–11767 (1992). https://doi.org/10.1103/PhysRevB.45.11749

43. R.L. de Kronig, On the theory of dispersion of X-rays. J. Opt. Soc. Am. JOSA. 12, 547–557 (1926). https://doi.org/10.1364/JOSA.12.000547

44. E. Haque, M.A. Hossain, Structural, elastic, optoelectronic and transport calculations of Sr₃SnO under pressure. Mater. Sci. Semicond. Process. 83, 192–200 (2018). https://doi.org/10.1016/j.mssp.2018.04.037

45. W. Khan, J. Minar, Theoretical study on optical and thermoelectric properties of the direct band gap α/β-Ca₂CdAs₂ pnictide semiconductors. RSC Adv. 4, 46791–46799 (2014). https://doi.org/10.1039/C4RA06700B

46. D.R. Penn, Wave-number-dependent dielectric function of semiconductors. Phys. Rev. 128, 2093–2097 (1962). https://doi.org/10.1103/PhysRev.128.2093

47. J. Islam, A.K.M.A. Hossain, Semiconducting to metallic transition with outstanding optoelectronic properties of CsSnCl₃ perovskite under pressure. Sci. Rep. 10, 14391 (2020). https://doi.org/10.1038/s41598-020-71223-3

48. C.M.I. Okoye, Optical properties of the antiperovskite superconductor MgCNi₃. J. Phys. 15, 833–841 (2003). http://dx.doi.org/10.1088/0953-8984/15/6/310

49. A. Hossain, M.K.R. Khan, M.S.I. Sarker, A systematic computational study of electronic, mechanical, and optical properties of Fe₁₅Co₂ alloy. J. Phys. Commun. 4, 045003 (2020). https://doi.org/10.1088/2399-6528/ab843b

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