Investigations of fundamental physical and thermoelectric properties of methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) perovskites

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Abstract

We have explored structural, electronic, optical and thermoelectric properties of cubic phase CH$_3$NH$_3$PbI$_3$ hybrid organic–inorganic perovskite by the first principles calculation based on density functional theory. Density of States (DOS) and band structure calculations shows that CH$_3$NH$_3$PbI$_3$ has direct band gap in R symmetry point (0.5 0.5 0.5) about 1.601 eV. A previous experimental and theoretical result agrees well with structural and electronic parameters. The optical properties such as dielectric constant, dispersion and absorption parameter have also been calculated. We have also performed thermoelectric properties like as Seeback coefficient, electrical conductivity, power factor, thermal conductivity and figure of merits at different temperature. The observed result shows that this material is optically active in the visible and ultraviolet regions, and therefore can be successfully used for optoelectronic devices.

1. Introduction

Hybrid organic–inorganic perovskites shown great possibilities in the area of light-harvesting material, because of their remarkable optical and electrical properties i.e. (large absorption, direct band gap and high carrier mobility) [1–3]. Perovskites are represented by the structure of this formula ABX$_3$ [4]; where A is monovalent cation (Cs$^+$) or an organic molecular (CH$_3$NH$_3$), B represent metal cation Pb$^{2+}$ or Sn$^{2+}$ and monovalent anion (Cl$^-$, Br$^-$ or I$^-$) is represented by X. Many hybrid organic–inorganic perovskites have been studied up to now; but for photovoltaic devices CH$_3$NH$_3$PbI$_3$ is the most favorable material. CH$_3$NH$_3$PbI$_3$ have some advanced properties such as the long diffusion length (>175 lm) and high power conversion efficiency up to 20% to 22% [5–7]. In addition to this CH$_3$NH$_3$PbI$_3$ perovskites has been used in some other fields such as a laser, photodetector and light emitting diodes demonstrating their potential application outlook [8, 9]. The essential property of hybrid organic–inorganic perovskites is their phase complexity from cubic, tetragonal, orthorhombic and monoclinic polymorphs. The transition temperature for orthorhombic (space group -Pna2$_1$) to tetragonal (space group- P4/mmm) is 161.4 K and finally from tetragonal to cubic (space group- Pm_3m) the transition temperature is 340.4 K. The main reason for phase transitions is a change in temperature, pressure and applied field [10]. Radi et al [11] have been explored six different perovskite structure i.e. CsPbX$_3$, CH$_3$NH$_3$PbX$_3$, (X = Cl, Br, I), and RbPbX$_3$ using some necessary modification in PBE-mBJ parameters and calculated structural and electronic properties with or without spin–orbit coupling. Recently, Lang et al [12] and Yuan et al [13] have studied that band gap and lattice constant depends upon A, B and X in perovskite structure. They have observed that, as A increases from inorganic (Cs) to organic molecules (CH$_3$ NH$_3^+$ or NH$_3$CHNH$_3^+$) and X changes from Cl$^-$ to Br$^-$ to I$^-$ anion lattice constant increase and B varies from Sn$^{2+}$ to Pb$^{2+}$ band gap increase. Castelli et al [14] and Ren et al [15], have observed that the position and orientation of CH$_3$NH$_3^+$ have direct consequence on structural and electronic properties of CH$_3$NH$_3$PbI$_3$, in its orthorhombic, Tetragonal and cubic phase. Egger et al [16] and Li et al [17] have incorporated the dispersion
corrected DFT theory by applying Vdw interaction into semi-local density functional theory and corrects the lattice parameter and affect the atomic structure of MAPbI₃.

In this paper, we have focused on cubic hybrid organic-inorganic perovskite CH₃NH₃PbI₃, and presented the results of first principles calculations for their structural, electronic and optical properties. The outline of the paper is as follows. In section 2 we have given a brief review of the computational scheme. The structural, electronic, optical and thermolectric properties have been described in section 3; while the summary and conclusions have drawn in section 4.

2. Computational details

The first principles calculations have been performed by the linearized augmented plane wave (LAPW) method as the theoretical account of density functional theory by solving Cohen-Sham equations [18] and implemented in the Wien2k package [19] to obtain the structural, electronic and optical properties of cubic hybrid organic-inorganic perovskite CH₃NH₃PbI₃. In this method, each atom of a unit cell is enclosed by a muffin-tin sphere, there are basic two regions one region is interior of these muffin-tin spheres and the other is interstitial region. Generalized Gradient Approximation (GGA) by Perdew–Burke–Ernzerhof (PBE) of exchange-correlation potentials have used for calculations [20]. To expand the spherical harmonics in the atomic sphere the value of \( l_{\text{max}} \) is taken as 10. A cubic unit cell, where Pb atoms are present on the corner of the cube and they are octahedrally coordinated with iodine atoms; while organic molecules CH₃NH₃ present at the center of the cube with a proper orientation of C–N bond as shown in figure 1. The muffin-tin radii of a different atomic sphere are 2.5\( a_0 \) for Pb and I, 1.27\( a_0 \) for N, 1.34\( a_0 \) for C and 0.68\( a_0 \) for H respectively; where \( a_0 \) is the Bohr radius. The 6s₂ 6p₂ for Lead and 5s₂ 5p₅ for Iodine are considered as valence electron. The value of RK\(_{\text{max}}\) (the product of RMT\(_{\text{min}}\) and K\(_{\text{max}}\)) was chosen to be 3, because of the smallest muffin-tin radius of the Hydrogen atom and K\(_{\text{max}}\) refers to the largest K-vector in the first Brillouin zone. A small k-mesh of 125 k points was used and 5 \times 5 \times 5 Monkhorst–Pack grid [21] has been selected for sampling the Brillouin zone.

The cutoff energy is set to –6.0 Ry. The atomic coordinate of all the atoms are in a fully relaxed position using the MSRL a optimization method. The SCF cycle are considered to be converged when the energy difference and the integration of absolute charge density difference between subsequent iterations is less than 10⁻⁵ Ry and 0.001 Coulomb/formula unit respectively. The atomic positions are optimized by minimizing the forces to 1 mRy/Å, acting on the atoms. A little change in the band structure will be seen, if we increase energy cutoff and k-points. The optical properties have been calculated by using Kemer-Kronig relation, for this denser k-mesh of 21 \times 21 \times 21 k-points in the Brillouin zone. The thermolectric properties like Seebeck coefficient, electrical conductivity, thermal conductivity, power factor and figure of merits have also been calculated using the BolzTraP code [22] within the rigid band approximation [23]; that solves the semiclassical Boltzmann transport equation [22] under the constant scattering time approximation (\( \tau \)). To calculate correct thermolectric properties, much denser k-mesh of 21 \times 21 \times 21) has been used. All the thermolectric properties have been calculated on carrier concentration range 10¹⁸–10¹⁹ cm⁻³ (p for hole and n for electron) at different temperature.

Figure 1. A schematic structure of (a) CH₃NH₃PbI₃ in cubic phase. A unit cell contains Lead (Light gray), Iodine (Violet), Hydrogen (white), Nitrogen (light blue), and carbon (brown).
3. Results and discussion

3.1. Structural properties

We start with a series of cycles to get lattice parameters and total energy values for the relaxed structure. Lattice constants versus total energy per unit cell is fitting into Birch-Murnaghan equation of state \[ E(V) = E_0 + \frac{9V_0B_0}{16} \left( \left( \frac{V_0}{V} \right)^{2/3} - 1 \right)^3 B'_0 + \left( \frac{V_0}{V} \right)^{1/3} - 1 \right)^2 \times \left[ 6 - 4 \left( \frac{V_0}{V} \right)^{2/3} \right] \]

The value of lattice constant \( a \) is 6.32 Å and shows very good agreement with experimental and other reported data \([25, 26]\).

3.2. Electronic properties

The band structure curve has been plotted between energy function and k vector in the first Brillouin zone. The curve gives some important information regarding the behavior of electronic nature of material being metal or nonmetal and type of energy gap being direct or indirect. The electronic band gap can be determined by the difference between the electronic states at the valance band maximum (VBM) and conduction band minimum (CBM). Thus, according to plotted band structure curves in figure 3, it shows that this material is a direct band gap semiconductor. The calculated band gap for CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} along the high symmetric point of Brillion zone is 1.601 eV with the GGA–PBE (without SOC) exchange-correlation potential. Hence, we have employed GGA–PBE (without SOC) exchange-correlation potential for calculation of all other properties of this material. It is direct on the R point (0.5, 0.5, 0.5) and is good agreement with the reported experimental or theoretical studies \([27–29]\). In addition to that, at M symmetric point (0.5, 0.5, 0) another direct band gap can be seen with the magnitude 2.48 eV. We have shown comparative analysis of band gap and lattice constant for different methods in table 1.

The total and partial density of states calculation for CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} cubic perovskites structure has been shown in figure 4. By comparing the TDOS and PDOS plot with the band structure a good adaptation has been seen. Each term of TDOS can be explain by dividing it into three regions, lower valence band region from (−9.5 to −4 eV) major contribution of Pb–6s, CH\textsubscript{3}NH\textsubscript{3}—s and CH\textsubscript{3}NH\textsubscript{3}—p orbitals. The upper valence band from −3.9 to 0 eV there is minor contribution of I–5p and Pb–6s orbitals in this region hybridization between these orbitals has been seen which recommend the covalent bond contributions in this region. A conduction band minimum as shown in figure 4 is associated to the Pb–6p orbitals and a small part of Iodine. The conduction band minima lie immediately upper to the valence band maxima after a gap of 1.601 eV. The region contains the overlapping of Pb–p and I–p orbitals besides to a negligible contribution of p states of the CH\textsubscript{3}NH\textsubscript{3} cation. The above plotted curve shows that, electronic levels of organic cations (CH\textsubscript{3}NH\textsubscript{3}\textsuperscript{+}) are preset in the valence band maxima and conduction bands minima but they do not contribute in any transition.
Borriello et al\cite{30} have been found that the variation of electronic properties of hybrid halide perovskites, because of the electronic structures and tilting of the PbI$_6$ octahedral network and explained that there is not any important contribution of organic molecules in the band gap formation and variations. However, Brivio et al\cite{25} and Motta et al\cite{31} suggested that on CH$_3$NH$_3$PbI$_3$ thin film the positioning of organic molecules has a momentous impact and it would be lead to changing the band gap and crystal constant. Ke et al\cite{32} have been concluded in their experimental result, after changing the concentration of organic cation during the formation of CH$_3$NH$_3$PbI$_3$ film the optical band gap of film changes from direct (1.52 eV) to indirect (2.64 eV).

**Figure 3.** Energy band structure of CH$_3$NH$_3$PbI$_3$ using GGA-PBE Calculation without SOC calculations. The size of the circle shows the contribution of particular orbit electrons in the band gap. A single point denotes zero contribution. (a) Pb 6p, (b) I 5p, (c) Pb 6s and (d) CH$_3$NH$_3$PbI$_3$ (with electron and hole concentration region. The energy zero corresponds to VBM. The symmetry points are used (R = 0.5, 0.5, 0.5; Γ = 0, 0, 0; M = 0.5, 0.5, 0; X = 0.5, 0, 0).
Table 1. Calculated lattice constant $a$ (Å) and band gap $E_g$ (eV) values of CH$_3$NH$_3$PbI$_3$ compared with available experimental and theoretical data.

| Present work $a$ (Å) | Other work $a$ (Å)  | Experimental work (Å) | Present work $E_g$ (eV) | Other work $E_g$ (eV) | Experimental work |
|----------------------|---------------------|------------------------|-------------------------|-----------------------|-------------------|
| 6.32                 | 6.29 (PBE-sol) [25] | 6.31 [11]              | 1.605 (GGA-PBE)         | 1.38 (HSE06) [25]    | 1.5–1.6 [11]      |
| 6.02 (LDA) [1]       |                     |                        | 1.537 (GGA-WC)         | 1.33 (LDA) [1]       |                   |
| 6.38 (PBE-vdW) [16]  |                     |                        | 1.527 (LDA)            | 1.115 (PBE) [13]     |                   |
| 6.21 (HSE) [13]      |                     |                        | 0.803 [GGA-PBE(SOC)]   | 1.662 (HSE) [13]     |                   |
|                      |                     |                        | 1.75 [TB- mBJ] (SOC)   |                       |                   |
3.3. Optical properties

Optical properties play an important role to understand the nature of material whether it can be used as optoelectronics device or not. We can explain the interaction of electron with the incident photon with the help of time dependent perturbation theory of ground state electronic state. The complex dielectric function describes the optical response of a material on incident electromagnetic radiation.

\[ \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \]

Where \( \varepsilon_1(\omega) \) explain the dispersion of incident radiation and \( \varepsilon_2(\omega) \) corresponds to the energy absorbed by the material. The imaginary part of dielectric function i.e. \( \text{Im}\varepsilon(\omega) \) can be written as [33].

\[ \text{Im}\varepsilon(\omega) = \frac{4\pi^2}{\omega^2 m^2} \sum_i \int \langle \hat{q} M | j^2 \rangle f_i(1 - f_i) \delta(E_f - E_i - \omega) dk \]

Where M is the dipole matrix and \( i \) and \( j \) are initial and final stats respectively, \( f_i \) is the Fermi distribution function for \( i \)th state; \( E_i \) is the energy of electron in the \( i \)th state and \( \omega \) is the frequency of incident photon. The real part of dielectric function can be calculated by Kramers–Kronig relation [33].

\[ \text{Re}\varepsilon(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \]

The observed optical spectra are connected with the band structure because it accounts the electronic transition from valence band maxima to conduction band minima along high symmetry direction of brillions zone. The knowledge of dielectric function (i.e. both the real and imaginary parts) permits the calculation of important optical parameters. In the present work we report some of such parameter like reflectivity \( R(\omega) \), absorption coefficient \( \alpha(\omega) \), optical conductivity \( \sigma(\omega) \), extinction coefficient \( k(\omega) \) and etc.as functions of the photon energy in the range of 0–24 eV. Reflectivity spectrum is derived from Fresnel’s formula [34];

\[ R(\omega) = \left| \frac{\varepsilon^{1/2}(\omega) - 1}{\varepsilon^{1/2}(\omega) + 1} \right|^2 \]

We have calculated the optical conductivity \( (\sigma) \), absorption coefficient \( (\alpha) \) and electron energy loss \( (E_{\text{loss}}) \) function, using the following relation [35];

\[ \text{Re}[\sigma(\omega)] = \frac{\omega\varepsilon_2}{4\pi} \]

\[ \alpha(\omega) = \sqrt{2}(\omega)(\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega))^{1/2} \]

\[ -\text{Im} \left( \frac{1}{\varepsilon} \right) = \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)} \]

Extinction coefficient \( k(\omega) \) and refractive index \( n(\omega) \) have been calculated by using dielectric function as follows [35].
Figures 5(a) and (b) shows nearly same pattern; little differences are in height of the peaks, indicating very small optical anisotropy in the material. From figure 5(b) the calculated value of threshold energy or critical points of $\varepsilon_2(\omega)$ occurs at 1.62 eV that describes the optical band gap of the material; which is close to the calculated band gap that shows the accuracy of the current results. The calculated optical band gap is good agreement with over experiment result [36]. Beyond this energy direct transition occurs and after that spectra increases sharply and gets two sharp essential peaks around 3.17 (391.12 nm) and 6.57 eV (188.71 nm) respectively. Figure 5(a) represent real part $\varepsilon_1(\omega)$, at $\omega = 0$ it shows the value of dielectric constant, that is 6.1. Demchenko et al [37] have reported a comparative analysis between experimental ellipsometry measurements of dielectric function with the DFT calculated result using GGA/LDA potential, and calculated dielectric constant is good agreement with experimental result.

The curve increases from $\omega = 0$ and reaches to top value 8.83 at 3.256 eV after this its value slightly decrease from its resonance value and turn out to be negative in the regions from 9.047 eV to 12.802 eV and 13.156 eV to 13.319 eV. According to Penn’s model [38] $\varepsilon_1(0)$ rises with the decrement in the electronic band gap.

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

Where $\hbar \omega_p$ and $E_g$ are the plasma frequency and energy band gap.

The refractive index $n(\omega)$ are calculated and they are presented in figure 6. The obtained static refractive index $n(\omega \to 0)$ is equal to 2.47. The shape of refractive index spectra is same as real part of dielectric functions by the relation $n(\omega) = [\varepsilon_1(\omega)]^{1/2}$. The maximum refractive index $n(\omega)$ is obtained 3.03 at an energy of 2.272 eV respectively as previously discussed direct inter band transition occurred from valence band to conduction band in the system in this region. CH$_3$NH$_3$PbI$_3$ is no longer active as a transparent material in the higher energy region because the refractive index is less than unity. The observed value of refractive index is good agreement with the experimental and other theoretical data [39].

Optical conductivity is an important optical parameter for conduction of electron due to an applied electromagnetic field. Figure 7(a) show the spectra of optical conductivity of CH$_3$NH$_3$PbI$_3$ at different energies. The optical conductivity starts after 1.70 eV and beyond this, spectra increases and reaches up to is maximum value around 3.002 at 3.27 eV. As the material has high absorption coefficient means that they absorb more photon which excite electron from valence band to conduction band. The calculated absorption coefficient
against the photon energy is shown in the figure 7(b). The three outstanding peaks are observed about 3.76, 9.292 and 14.62 eV, and the absorption is almost negligible in the region from 0 to 1.60 eV. At energy value 9.292 eV (wavelength 133 nm) we get maximum value of absorption coefficient. At photon energies above 15.33 eV, the absorption coefficient sharply decreases.

The computed reflectivity spectra of CH3NH3PbI3 Perovskites are represented in figure 8(a). From the curve, a protuberant peak is noticed around 3.27 eV. Clearly, the zero frequency reflectivity of CH3NH3PbI3 is 17.5% which remains nearly constant up to 1.5 eV. This increment is sustained up to 9.34 eV and afterward decreases from energy range 10.00 to 25 eV. The maximum value of reflectivity $R(\omega)$ is 35.03% at 3.5 eV.

Noticeably, from the absorption and reflection spectra relation, if absorption is maximum then obviously reflectivity will be negligible or minimum. In this region material substantially absorbs light and it cannot effectively reflect light in the same span. Remarkably, the studied material shows up to 83% absorption at the zero photon energy because at that point reflectivity is 17%.

$E_{\text{Loss}}(\omega)$ represent the energy loss of a fast moving electron inside the material. The peaks in $E_{\text{Loss}}(\omega)$ represent the characteristic, combined with the plasma resonance and the corresponding frequency is the called plasma frequency ($\omega_p$). From the computed spectra figure 8(b), the observed plasma frequency is 18 eV. Behaviour of the material whether it is metal or dielectric can be evaluated by plasma frequency below which material is metallic and above which it is a dielectric.
3.4. Thermoelectric properties

Thermoelectric materials have mesmerized much interest because of their proficiency of converting heat directly into electricity or vice versa. The enactment of solar thermoelectric devices depends on the adeptness of both light absorption and thermoelectric energy conversion. Those materials which have the large optical absorption coefficient may be used to adequately collect sunlight and transform it into heat. One of the thermoelectric property, dimensionless figure of merit (ZT) represent the conversion efficiency between heat and electricity of a thermoelectric material.

\[ ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_l} \]

Where \( S \) is Seebeck coefficient (Thermo power), \( \sigma \) absolute temperature (\( T \)) and electrical thermal conductivity (\( \kappa_e \)) and lattice thermal conductivity (\( \kappa_l \)), \( S^2 \sigma \) is known as the power factor. By the above formula we can prognosticate that higher ZT can be achieved by decreasing thermal conductivity and increasing the power factor. In this section, carrier concentration and temperature dependent thermoelectric properties of CH\(_3\)NH\(_3\)PbI\(_3\) are studied by solving the Boltzmann transport equation as implemented in the BoltzTraP code. To justify the region of electron and hole concentration in band structure curve, from Boltzmann theory \[40\]  

\[ E_e = E_f = kT \ln \left( \frac{N_e}{n} \right) \]

\[ E_f = E_v = kT \ln \left( \frac{N_v}{p} \right) \]

where \( k \), \( T \), \( N_v \), \( N_e \), \( n \), \( p \) are Boltzmann constant, room temperature (300 K), effective density of state of valence and conduction band, concentration of electron and hole (\( 10^{18} \)-\( 10^{19} \) per cm\(^3\)) respectively. The effective mass of electron and hole are \( m_e^* = 0.25 m_0 \) and \( m_h^* = 0.12 m_0 \), where \( m_0 \) = mass of electron \[41\]. The region of \( 10^{18} \)-\( 10^{19} \) electron and hole concentration is shown in figure 3(d). The calculated properties are the thermopower or Seebeck coefficient (\( S \)) in \( \mu \text{V/K} \), the electrical conductivity (\( \sigma / \tau \)) in \( \Omega^{-1} \text{m}^{-1} \text{s} \), the power factor \( (S^2 \sigma / \tau) \) in \( \text{W/mK}^2 \) and electrical component of thermal conductivity \( (\kappa_e / \tau) \) in \( \text{W/mKs} \) as functions of carrier concentration (\( 10^{18} \) to \( 10^{19} \)) on at different temperature range 300 K to 800 K.

3.4.1. Thermopower or Seebeck coefficient (\( S \)) and electrical conductivity (\( \sigma / \tau \))

In Seebeck effect a potential difference is developed between two successive contacts when there is a temperature gradient between them. From higher to lower temperature end, due to the movement a potential difference in micro volt per Kelvin is developed between the two ends. This voltage depends upon the nature of materials and temperature gradient between the ends. From the various previous studies \[42, 43\], it is evident that the thermopower increases with decreasing the carrier concentration i.e. Pisarenko behavior. In good thermoelectric material, \( 10^{18} \) to \( 10^{19} \) cm\(^{-3}\) carrier concentrations is an optimum working region \[44\]. Seebeck coefficient or therompower can be completely determined from the band structure by using CSTA. Figure 9(a),
shows the calculated Seebeck coefficient over a wide range of carrier concentrations ranges from $10^{18}$ to $10^{19}$ per cm$^{-3}$ at temperature range from 300 K to 800 K for CH$_3$NH$_3$PbI$_3$.

Figure 9(a) shows at carrier concentration $n = 10^{18}$ cm$^{-3}$, at temperature $T = 300$ K, 600 K, 800 K, the Seebeck coefficient is $-600 \mu$V K$^{-1}$, $-700 \mu$V K$^{-1}$, $-800 \mu$V K$^{-1}$ respectively. For the same temperature, the magnitude of Seebeck coefficient decreases as carrier concentration increases, but with for the same carrier concentration in this paper, above $10^{18}$ cm$^{-3}$ the Seebeck coefficient decreases with the increase of T. Similarly from figure 9(b) at $p = 10^{18}$ at temperature T = 300 K, 600 K, 800 K, the Seebeck coefficient has been observed approximately $600 \mu$V K$^{-1}$, $700 \mu$V K$^{-1}$, $800 \mu$V K$^{-1}$ respectively. From the above plotted curves magnitude of Seebeck coefficient is almost same either with n type or p type carriers.

Figures 10(a) and (b) represent the evaluated electrical conductivity versus the relaxation time ($\sigma/\tau$) over the carrier concentrations ranges from $10^{18}$ to $10^{19}$ per cm$^{-3}$ at temperature range from 300 K to 800 K for CH$_3$NH$_3$PbI$_3$. In the above plotted data, it is evident that the electrical conductivity is decreases with temperature for both n and p type carrier density.

3.4.2. Power factor and thermal conductivity

The power factors divided by relaxation time $S^2/\sigma$ of CH$_3$NH$_3$PbI$_3$ as a function of doping concentrations are shown in figures 11(a) and (b) for n and p type charge carriers. In the plotted curve it can be seen that, there exist a peak value within the carrier concentration range, which proposes that the thermoelectric performance of the CH$_3$NH$_3$PbI$_3$ compound can be optimized by appropriate doping concentration. The calculated power factor $S^2/\sigma$ as a function of n and p type doping, increases from 400 to 800 W/mKs as temperature increases from 300 to 800 K for fix electron concentration and 300 to 600 K with fix hole concentration $5 \times 10^{18}$ cm$^{-3}$ respectively. The power factor can be experimentally controllable by increasing or decreasing the doping concentration. For the good thermoelectric material the power factor should be minimum for given carrier concentration. The thermal conductivity has been shown in figures 12(a) and (b), the observed value vary from $1 \times 10^{13}$ to $2 \times 10^{13}$ W m$^{-1}$ K$^{-1}$ on temperature range from 300 K to 800 K at constant $10^{18}$ cm$^{-3}$ for n type doping and $0.2 \times 10^{10}$ to $1.5 \times 10^{13}$ W/mKs for p type doping respectively. As we increase the operating temperature and constant the carrier concentration electronic component of thermal conductivity increases.
we know that the total thermal conductivity is the combination of lattice ($k_l$) and electronic thermal conductivity ($k_e$).

$$k = k_e + k_l.$$

We have studied only electronic part and ignore the lattice thermal conductivity, because lattice thermal conductivity part cannot be study by BoltzTraP code. From the plots, it has been cleared that electronic thermal conductivity depends on temperature and carrier concentration.

### 3.4.3. Figure of merits (ZT)

To get high ZT is important disciplined task, since high ZT is a strongly counter indicated transport property. To get high ZT, there are following requirements; (1) to get high mobility and low thermal conductivity, resulting that strong scattering of phonon and week scattering of charge carrier; (2) due to high mobility of charge carriers and high thermopower; (3) high melting point and low thermal conductivity and at last; (4) effectively controlled doping. Although there is no limit is found for ZT, but many authors\[45\] suggested that for a good thermoelectric device the maximum value of ZT is approximately 1.0. In this work we have only electrical thermal conductivity so that we only get the electrical figure of merits (ZT) because lattice thermal conductivity cannot be calculated using BoltzTraP and other theoretical study. Form the figures 13(a) and (b), we have seen that electronic ZT increases with increasing of temperature for CH$_3$NH$_3$PbI$_3$. It has been observed due to the increasing temperature, of course, but as the above mentioned requirement also have to be fulfilled i.e. thermopower increases with T, the electronic thermal conductivity have to be low and the controlled doping which is $10^{18}$ cm$^{-3}$ in this case. From figures 13(a) and (b), at electron concentration $n = 10^{18}$ cm$^{-3}$, the electronic ZT increases from 0.92 to 0.96 and for hole concentration $p = 10^{18}$ cm$^{-3}$ electronic ZT increases from 0.90 to 0.95; when temperature increases from 300 K to 600 K. It is also noticed that as further increment of carrier concentration either n or p the ZT is successively decreases from 0.96 to 0.80 for n type doping and 0.95 to 0.70 for p type doping. From the above figures, it has been concluded that CH$_3$NH$_3$PbI$_3$ is a good thermoelectric material in the temperature range $10^{18}$ cm$^{-3}$ at room temperatures.
4. Conclusions

First principle calculations have been performed to study and compare the various properties of cubic perovskite CH$_3$NH$_3$PbI$_3$ compound by FP-LAPW method within GGA-PBE approximations. It was found that the studied material has a direct-band gap at the $R(0.5\ 0.5\ 0.5)$ symmetry point about 1.601 eV that is very close to other theoretical and experimental results. It is reported that, the static dielectric coefficient and refractive index for this compound are $\varepsilon_1(0) = 6.00$ and $n(0) = 2.50$ respectively. The thermoelectric properties were anticipate and discussed in details by using BoltzTrap code through the semi-classical transport theory, in addition to the constant relaxation time approximation and rigid band approximation. The transport properties like Seebeck coefficient ($s$), electrical conductivity over relaxation time ($\sigma/\tau$), electronic thermal conductivity ($\kappa_e/\tau$) have been employed to calculate power factor and dimensionless electrical figure of merit ($ZT$), which endorses this compound as a potential thermoelectric material. We have noticed that the overall pattern of electrical figure of merit ($ZT$) clearly show that, increment of carrier concentration from $10^{18}$ to $10^{19}$ cm$^{-3}$ either n or p type the ZT is successively decreases from 0.96 to 0.80 for n type doping and 0.95 to 0.70 for p type doping at room temperature. The calculated thermoelectric properties indicate that CH$_3$NH$_3$PbI$_3$ is a very promising thermoelectric material at room temperature. Predominantly, CH$_3$NH$_3$PbI$_3$ organic-inorganic halide perovskites are propitious candidate for the photovoltaic applications, because from their optical absorption spectra have maximum value in the visible and near-UV span.

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Figure 13. The electrical figure of merits ($ZT$) of CH$_3$NH$_3$PbI$_3$ under different carrier concentration (a) n type (b) p type.
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