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High thermopower and birefringence in layered mercury-based halides



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ABSTRACT

This work presents a theoretical investigation of mercury-based halides in both bulk and monolayer form. These compounds are direct bandgap semiconductors in bulk and monolayer form as it is evident from the analysis of structural and electronic properties. Birefringence values have been used to ascribe anisotropic optical properties, which may host future opto-electronic device applications. The values of mobilities for both the carriers in HgI₂ are consistent with the experimental values. The low value of lattice thermal conductivity and favorable carrier mobilities provide a better scope for thermoelectric properties. The least bandgap of HgI₂ further enables thermoelectric applications, and the thermopower is found to be high with a value of 580 μ V/K for holes and nearly 320 μ V/K for electrons. The thermoelectric efficiency for holes is quite appreciable with a figure of merit *zT* around 0.5 at 300 K for a carrier concentration of 10¹⁹ cm⁻³. In case of monolayers, the thermopower of HgI₂ monolayer is found to be higher than its bulk counterpart. Our findings show that these compounds have robust transport and optical properties, which await future experimental verifications.

1. Introduction

Layered materials accentuated the concept of tunability by fabricating monolayers to multilayers with benefits for novel diverse applications creating a new avenue for exploration. Properties displayed by bulk vary substantially in layers due to the confinement of charge carriers and photons. Mercuric halides (HgX2, X = I, Br, Cl) gained a heightened interest from several decades due to their distinguishing usage. These halide-based compounds are generally wide-bandgap type semiconductors, possessing various optical applications. Due to its large atomic masses and high resistivity, HgI2 is well suited for use as a gamma and X-ray detector [1,2]. Molecular monomers, dimers, trimers of mercuric halides, especially mercuric chloride, were studied using first principle calculations with both relativistic and non-relativistic effects giving us a detailed structural analysis on bond angles, bond lengths, and coordination numbers of their structures [3-5]. Cheng et al. studied the band spectrum and optical response with inclusion of spin orbit coupling in HgI₂ using nonlocal pseudopotential methods [6]. Ahuja et al. [7] used the linear muffin-tin orbital method to enumerate the electronic structure of HgI₂ devoid of geometrical approximations. A comprehensive investigation of reflectivity spectrum and anisotropic frequency-dependent dielectric function were also derived using selfconsistent potential. Xu Bin and Lu Jian [8] studied linear optical properties along with electronic structure calculations using the fullpotential linearized augmented plane wave method, giving a more meticulous analysis of HgI2. Some further first principle calculations in search of mid-infrared nonlinear optical materials for laser applications found $HgBr_2$ to be favorable with a high laser damage threshold [9,10]. Xuemei et al. [11] reviewed the correlation between structures and nonlinear optical properties to confirm it as a good infrared nonlinear optical crystal. Compton profiles of HgI2 and HgBr2 were studied by Ahmed et al. [12] using a high energy Compton spectrometer, in addition to this, the photo-luminescence and detection properties were also discussed, making these mercuric halides a more beneficial material. High-pressure X-ray diffraction studies were done on HgI₂ to confirm phase transition from tetragonal to orthorhombic phase [13]. Karmakar et al. [13] used high-pressure photoluminescence measurements to confirm the bandgap of different phases. Till this point, we have discussed the optical aspects of halide-based materials, but these materials might also possess thermoelectric applications. Numerous previous studies are evident for projecting a material to possess both optical and thermoelectric applications, and a few of them are discussed here. Alkali-based halides were studied for optical and thermoelectric properties by Mohammad et al. [14] with a reported *zT* value of 0.82 using the first-principles. The halide perovskites were also explored for their

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Optimized parameters of HgX_2 (where, X = Cl, Br and I) along with experimental parameters.

Compounds	Experimental parameters			GGA+v	GGA+vdw			GGA			LDA					
	a (Å)	b (Å)	c (Å)	V (Å ³)	a (Å)	b (Å)	c (Å)	V (Å ³)	a (Å)	b (Å)	c (Å)	V (Å ³)	a (Å)	b (Å)	c (Å)	V (Å ³)
HgCl ₂	12.76	5.97	4.33	330.09	12.79	6.07	4.2	348.64	13.85	6.76	4.27	399.54	13.29	5.76	3.89	298.02
$HgBr_2$	4.62	6.80	12.44	391.20	3.93	7.28	13.28	399.13	5.03	7.01	13.64	481.03	4.17	6.77	11.97	337.90
HgI_2	4.37	-	12.42	237.30	4.27	-	12.67	247.53	4.51	-	14.05	286.32	4.35	-	11.84	224.11

optical applications like solar cell, photovoltaic cell, etc., [15,16] and later these are found to be a very good thermoelectric material [17–19]. The above-discussed previous studies together with a few more [20,21] motivated us to opt a series of mercury halides for their optical and thermoelectric properties. Although, a lot of first-principle calculations in different perspectives were already done for these mercuric halides in bulk, not much were explored in layer form. With this motivation we have explored the structural, electronic, optical and thermoelectric properties for mercury-based halides in both the bulk and layer form. Firstly, the computational methods are briefly discussed in Section 2, which is followed by results and discussion, and Section 5 summarizes the paper.

2. Computational methods

The pseudopotential method implemented in VASP (Vienna Abinitio Simulation Package) [22-24] is used to get the ground state properties. The electronic structure calculations were calculated using Full potential linearized augmented plane wave (FP-LAPW) method as equipped in the WIEN2K package [25]. The PBE-GGA (Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation) [26] was used to treat the exchange-correlation part of the potential. The energy convergence value is chosen up to 10^{-6} Ry to achieve self-consistency. As the traditional exchange-correlation functionals underestimate the bandgaps in semiconductors, Tran and Blaha modified Becke-Johnson (TB-mBJ) potential [27,28] was used for the calculations of electronic structure and optical properties of these compounds which give the bandgap values comparable to experimental values. The electronic structure properties have been calculated for ground state energy eigenvalues. Mobility was computed from electrical conductivity which was calculated using the Boltzmann transport theory implemented in BoltzTraP code [29]. To calculate the nearequilibrium thermoelectric coefficients, the Constant Scattering Time Approximation (CSTA) and Rigid Band Approximation (RBA) [30-32] have been used.

3. Results and discussions

3.1. Structural and electronic properties

HgCl₂ and HgBr₂ both crystallize in orthorhombic phase, former with space group Pnma (62) and latter with space group Cmc21 (36), whereas HgI_2 is tetragonal with the space group symmetry P42/nmc (137). Table 1 represents the optimized parameters along with the experiment values [33,34,13] and we find that the GGA+vdW parameters are consistent with the experimental values and also support the van der Waals nature in these compounds. The crystal structure of the investigated systems is shown in Fig. 1. Band structure calculations were performed using TB-mBJ functional, as shown in Fig. 2. These systems are wide bandgap semiconductors, as revealed through the band's plots and the bandgap values [Table 2]. It is vivid that TB-mBJ functional exhibits good accordance with experimental results, and the same has been taken up for further analysis. The calculated bandgap of HgI₂ is consistent with the bandgap value reported in earlier work done by Ahuja et al. [5]. Firstly, we would like to discuss the electronic properties of HgI₂ in detail. It is a direct bandgap semiconductor with a bandgap of nearly 1.7 eV, which is further improved up to approximately 2 eV with the inclusion of Tb-mBJ functional [Fig. 2(a)].

Table 2 Bandgaps in eV for HgX_2 (where, X = Cl, Br and I).							
Compounds	Without TB-mBJ	With TB-mBJ	Experimental				
HgCl ₂	2.80	4.31	-				
HgBr ₂	2.24	3.36	3.3				
HgI ₂	1.12	1.90	2.04				

The directional dependent analysis of bands infers that the bands in the conduction band region are more dispersive than that of the one lying in the valence band region along both the axes 'a' and 'c'. In HgI₂, Hg and I are forming a dimer since the outermost orbital 6s² of Hg contains two electrons. In the presence of iodine, this is splitting into $6s^1$ and $6p^1$. One is responsible for pp hybridization between Hg-p and I-p states lying in valence band region, and the other one is responsible for sp hybridization between Hg-s and I-p states lying in conduction band regions beyond 3 eV. These hybridizations are responsible for the covalent nature of bonding in HgI2. This hybridization pattern is further confirmed by the density of states (DOS) analysis and is in good accord with the earlier reported one [12]. To understand the orbital contribution near the Fermi level, we have plotted the total density of states along with the partial contribution [Fig. 2(d)], and supports the wide bandgap semiconducting nature. I-p states and Hgs states are dominating in the valence and conduction band region respectively, and the same are contributing most to the total density of states. We have also calculated the electronic properties of two other mercury halides ${\rm HgCl}_2$ and ${\rm HgBr}_2.$ The band structure of ${\rm HgBr}_2$ is given in Fig. 2(b, e). The band's profile in the conduction band region near the Fermi level is similar to what we discussed for HgI₂. Hg-s and Br-p states are contributing most to the total density of states as seen from the DOS plots, creating bonding type molecular orbital corresponding to sp hybridization as discussed in earlier reports [12]. HgCl₂ is another orthorhombic system and a wide bandgap semiconductor with an initial bandgap of 2.72 eV, which further increases up to 4.14 eV using TB-mBJ functional. Hg-s and Cl-p states dominantly contribute to the energy levels and DOS formation. Similar orbital contribution and resulting hybridization can also be comprehended from the energy bands and DOS plots in Fig. 2(c, f). We have calculated the Born effective charge tensors for these compounds, and the same is given in supplementary Table 1 (Table S1). From the table, it is inferred that the Born effective charge for Hg and halide atom is not varying much from their nominal charges +2 and -1. As the covalent character increases, the Born effective charge increases. The acoustic sum rule is also satisfied, which confirms that the calculations are well converged.

3.2. Optical properties

Assessment of optical properties imparts a better understanding of the electronic structure of the compounds. To arrive at accurate optical properties, we have performed the calculations with 50000 kpoints using TB-mBJ functional. The optical properties of the investigated compounds have been computed using the dispersion relation of the complex dielectric function $\epsilon(\omega)$. The dispersion parameter $\epsilon(\omega)$ can be calculated using the band structure outputs. The real part of dielectric function $\epsilon_1(\omega)$ can be calculated from the imaginary part using Kramers–Kronig relation [35]:

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} P \int \frac{\omega' \epsilon_2(\omega)}{\omega'^2 - \omega^2} d\omega'$$



Fig. 1. The crystal structure (a) ${\rm HgI}_2$ (b) ${\rm HgBr}_2,$ (c) ${\rm HgCl}_2$ (d) ${\rm HgI}_2$ monolayer (e) ${\rm HgBr}_2$ monolayer.



Fig. 2. The electronic structure properties of HgI_2 in (a, d), $HgBr_2$ in (b, e) and $HgCl_2$ in (c, f).

Complex dielectric function, absorption coefficient, refractive index, reflectivity are plotted against photon energies to get an accurate understanding of a material's response to electromagnetic radiation. The real part of the dielectric function for all the compounds is shown in Fig. 3(a) and supplementary Fig. S1. The dielectric spectra are anisotropic and constant up to the photon energy equal to their bandgap, as the dielectric function characterizes the polarizability of any material in the presence of an electric field. We observe the transitions happening due to the internal electric field, and the peaks in the dielectric spectra are the evidence for the same. The dielectric constant values usually decrease with an increase in bandgap [Table 3]. The real part of dielectric spectra can be understood more in terms of the refractive index and the reflectivity of the system, and the same will be discussed later in this section. The imaginary part of dielectric spectra gives a better correlation of optical properties with the band structure of the system, and it also characterizes other properties like absorption spectra. The same is shown in Figs. 3(b) and S1. There is no absorption

noticed till the photon energy is equal to the bandgap of the system. The peaks observed in the absorption spectra correspond to the possible transitions. The absorption spectra are also anisotropic as transitions are not equivalent in all the crystallographic axes. The first transition is happening from valence band minimum to conduction band maximum as the systems are direct bandgap semiconductors. These transitions are based on selection rules, and whenever this criterion is fulfilled, the transition occurs at that value of photon energy.

The reflectivity, another important optical property, is also being calculated and is given in Fig. S3. The peaks in the reflectivity are due to interband transition [36]. Its value is highest when the real part of dielectric spectra is negative and shows metallic characteristics. As the energy increases, the value of reflectivity increases with oscillation and eventually leads to metallic behavior with shielding effect [37]. Another optical property called refractive index as a function of photon energy is given in Figs. 3(c) and S2. The value of the refractive index for HgI₂ is higher among all the compounds. The refractive indices



Fig. 3. The optical properties of HgI, (a) Dielectric spectra, (b) Absorption spectra, (c) Refractive indices. Birefringence of HgI, in (d), HgBr, in (e) and HgCl, in (f).

Table 3

Dialaatuia	o o moto mt	~ d	mafua atima	:	of Hov	(h ana	v _	C1	Da and I	a –
Dielectric	constant	and	refractive	maex		twhere.	A =	C.I.	br and i	
						(

Compounds	Dielectric constant		Refrac	tive ind	Birefringence		
	xx	уу	zz	n _{xx}	n_{yy}	n _{zz}	Δn
HgCl ₂	3.49	2.53	3.10	1.87	1.60	1.76	0.27
HgBr ₂	3.12	4.15	4.01	1.77	2.04	2.01	0.27
HgI_2	5.05	-	5.34	2.25	-	2.31	0.06

are written in Table 3, and we can see that their values are reducing with respect to the decrease in the size of the ions. The value of refractive indices is ranging between 2 to 3, which might be good for possible optoelectronic applications. Birefringence is one of the important intrinsic optical properties of a material which depends on the polarization and the propagation direction of incident light. HgI₂ is an optically uniaxial crystal and due to its tetragonal structure, it possess two refractive indices, one parallel to the optical axis and other perpendicular to the optical axis. On the other hand, HgCl₂ and HgBr₂ are biaxial crystals due to its orthorhombic structure. In biaxial crystals, the optic axes may or may not coincide with crystallographic axes. In our case, the optic and crystallographic axes are same as crystal symmetry is orthorhombic, and will lead to different values of static refractive indices along three crystallographic axes. The anisotropy in refractive indices causes the birefringence in these crystals. The birefringence values $(\Delta n_{ij} = n_{ii} - n_{jj})$ were plotted against the photon energy in Fig. 3(d, e, f) and the values are given in Table 3. HgCl₂ and HgBr₂ show high birefringence values of 0.27, which is comparable with other good birefringent materials like $SnCl_2$ (0.21), $SbCl_3$ (0.173), SnF_2 (0.191) [38]. These materials have wide applications in various optical devices such as retardation plates, polarization manipulators, optical modulators, optical sensors, crystal filters, etc.

3.3. Transport properties

To elaborate the transfer efficiency of carriers, we have calculated mobility scaled by relaxation time as a function of carrier concentration ranging from $10^{18}-10^{21}$ cm⁻³. The mobility is independent of carriers and almost temperature independent [Fig. 4(a, b), S4]. We approximated the relaxation time as 10^{-14} s so that the absolute value of mobility can be calculated. The value of mobility for HgI₂ is nearly 10 cm²/Vs for holes, and 100 cm²/Vs for electrons which is in good

accordance with the previously reported values [39]. The anisotropic nature is negligible here especially, for electrons. This trend of mobility can be connected to band dispersion. The carrier concentration is almost same along both the crystallographic axes, and small variation in band dispersion is leading to minor differences in values of mobility along 'a' and 'c' axes. If we move to other orthorhombic mercury halides, we have calculated the mobility along all three crystallographic axes. The value of mobilities is lying in the range of nearly $5 \text{ cm}^2/\text{Vs}$ to 300 cm²/Vs for holes in the case of HgBr₂ and display an appreciable anisotropy between 'a' and 'b' axes. This anisotropy is due to the presence of flattened bands along Γ -Y and dispersive bands along Γ -X in the valence band region. The former one is the cause for the reduction in the value of mobility, whereas the latter leads to higher mobility. The anisotropic factor is nearly 10. If we consider the electrons, the band's dispersivity is nearly the same in the conduction band region, which is reflected in the mobility plots for electrons. The mobility of HgBr₂ is shown in Fig. S4(a, b). Now, we will discuss the mobility scaled by relaxation time of HgCl₂ [Fig. S4(c, d)] and the values are lying in the range of 10^{14} cm²/Vs² to 10^{15} cm²/Vs² for holes, whereas it is 10^{15} $\rm cm^2/Vs^2$ to 10^{16} $\rm cm^2/Vs^2$ for electrons. In this case, the anisotropy is not as appreciable as seen in the case of HgBr₂. In summary, holes are more favorable for future device applications if one can study low dimension materials such as nanosheets, etc.

Lattice thermal conductivity (κ_l) is the ability of heat transfer between two points with dissimilar temperatures. As these compounds are semiconductors, the electronic thermal conductivity (κ_e) does not play a significant role, and the lattice thermal conductivity becomes more crucial. The lattice thermal conductivity for all three compounds is calculated using slack model [40] which gives the averaged value:

$$\kappa_l = A \frac{M\theta_D{}^3\delta}{\gamma^2 n^{2/3}T}$$

where *M* is the average atomic weight (in kg/mol), A is a proportionality constant which depends on γ , θ_D is the Debye temperature, δ^3 is the average volume of the unit cell (in m³), γ is the Grüneisen parameters obtained from Poison's ratio (ν):

$$y = \frac{3}{2} \left(\frac{1+v}{2-3v} \right)$$

The values of γ as calculated by the above formula are 2.096, 1.592 and 2.003 for HgCl₂, HgBr₂ and HgI₂ respectively. The coefficient A (in unit of W mol/kg/m²/K³) depends upon γ and is given by [41]:

$$A(\gamma) = \frac{5.720 \times 10^7 \times 0.849}{2 \times (1 - (0.514/\gamma) + (0.228/\gamma^2))}$$



Fig. 4. Mobility scaled by relaxation time of HgI_2 , (a) for holes (b) for electrons (c) phonon dispersion curve for HgI_2 (d) Average lattice thermal conductivity of HgX_2 , (X = I, Br, Cl).

The θ_D values are 91.33 K, 89.48 K and 88.65 K for HgCl₂, HgBr₂ and HgI2 respectively, which is very less compared to 164 K for PbTe, 190 K for PbSe [42]. The lattice thermal conductivity of these compounds exhibits typical behavior, i.e., it decreases with an increase in temperature. The average κ_l values are 0.27 W/mK, 0.23 W/mK, 0.09 W/mK at 300 K for HgI2, HgBr2 and HgCl2 respectively. The variation of κ_l with respect to temperature is shown in Fig. 4(d). Our calculated value of κ_l is considerably lower than the other well known thermoelectric materials i.e, 2.30 W/mK for PbTe, 2.64 W/mK for PbSe, 2.80 W/mK for PbS [42], 1.3 W/mK for Bi₂Te₃ [43]. The lattice thermal conductivity mainly depends upon two thermodynamic properties called the Debye temperature and Grüneisen parameter and can be understood better in terms of them. The low value of θ_D leads to a shorter mean free path, and the high value of γ causes a more anharmonic nature in the system. This shorter mean free path and anharmonic nature together enhance the phonon-phonon scattering, which further results in a low value of κ_1 as it varies inversely with γ and proportionally with mean free path. The phonon dispersion for HgI₂ is calculated to observe the phonon-phonon scattering in HgI₂ as an example case [Fig. 5(c)]. One can visualize the phonon gap between high- and low-frequency optical modes forming due to the differences in atomic masses of Hg and I atoms. The low-frequency optical phonon modes are highly interacting with acoustic modes. These interactions lead to more scattering, which further causes the reduction in the value of κ_l . The previous study on SnSe also explains the same, and κ_l value was reported to be 0.62 W/mK [42].

The low value of averaged κ_l along with varying band profile in HgI₂ with least bandgap among all the compounds motivated us to calculate the thermoelectric properties like thermopower, electrical conductivity, and power factor. The deformation potential theory [44] was used to compute the relaxation time (τ). We applied a uniaxial strain in the desired direction to calculate the deformation potential constant which is the rate of change in band edges with strain. The relaxation time is calculated using the relation given below [45]:

$$\tau = \frac{\sqrt{8\pi}\hbar^4 c_{ii}}{3(m^*k_BT)^{3/2}V_{DP}{}^2}$$

Here \hbar is the Planck's constant, c_{ii} is the elastic constant in the desired direction (in pascal), m^* is the effective mass, k_B is Boltzmann constant, T is the temperature in kelvin, V_{DP} is deformation potential constant.

$$V_{DP} = \frac{dE_{edge}}{d\alpha}$$

Here E_{edge} is the energy at the valence band maximum or conduction band minimum, and α is the uniaxial strain along the direction of the lattice vector. The values of relaxation time for different temperatures and axis are given in Table 4. The values of relaxation time at 300 K are of the order of 10^{-14} s⁻¹ for holes and 10^{-13} s⁻¹ for electrons. The thermoelectric properties are calculated for carrier concentration ranging from 1×10^{-18} to 1×10^{-21} . Fig. 5(a, d) illustrates the thermopower as a function of carrier concentration for different temperatures. The magnitude of thermopower decreases with carrier concentration, whereas it increases with temperature. Its magnitude is nearly 580 $\mu V/K$ for holes and 320 µV/K for electrons at room temperature, implying higher thermopower for holes than that of electrons with a difference of 250 µV/K. The holes show a nearly isotropic nature in thermopower plots and turn out to be isotropic at 700 K, whereas the electrons are isotropic even at room temperature. The absolute value of other thermoelectric coefficient called the electrical conductivity of HgI₂ is in the order of 10³ for holes and 10⁴ for electrons. The anisotropy seen in the electrical conductivity is due to the varying band dispersion along different axes as we discussed in the electronic structure properties. The power factor $(S^2\sigma)$ is also computed and is given in Fig. 7(c, f). The power factor is found to be 0.001 W/mK^2 along x-direction, 0.0018 W/mK² in z-direction for holes and 0.003 W/mK² along xdirection, 0.008 W/mK² along z-direction for electrons at 300 K. As the power factor is a combined effect of both the thermopower and the electrical conductivity, the anisotropy is high especially, for electrons which are good for low dimension applications. The power factor values in our case are comparable with the values for the previously studied compounds [46]. A material's efficiency for thermoelectric applications is justified through a dimensionless quantity called the figure of merit $zT = \frac{S^2\sigma}{(k_l+k_e)}T$, where *S* is Seebeck coefficient, σ is electrical conductivity, T is temperature, and k_l and k_e are the lattice and electronic contribution to the thermal conductivity respectively. The



Fig. 5. HgI2: Thermopower (a, d) Electrical conductivity (b, e) Power factor (c, f) as a function of concentration.

Table 4

Relaxation time τ for figi, in s	Relaxation	time	τ	for	HgI ₂	in	s^{-1}	۰.
---------------------------------------	------------	------	---	-----	------------------	----	----------	----

Temperature	2-avis		c-avis		
remperature	Holes	Electrons	Holes	Electrons	
300 K	2.8e-14	1.203e-13	6.43e-14	4.2e-13	
500 K 700 K	1.3e–14 8.08e–15	5.59e–14 3.37e–14	2.99e-14 1.8e-14	1.96e–13 1.18e–13	

electronic thermal conductivity is calculated using Wiedemann-Franz law: $k_e = L\sigma T$, where L is the Lorenz number, $2.4 \times 10^{-8} J^2 K^{-2} C^{-2}$ for free electrons. For HgI₂ the calculated k_e values at 300 K are: 0.37 W/mK and 0.6 W/mK for holes and 2.24 W/mK and 4.31 W/mK along 'a' and 'c' direction respectively. The average value of lattice thermal conductivity is already calculated using Slack model. Due to semiconducting nature of HgI₂, the power factor value is taken at a optimum carrier concentration of $10^{19} cm^{-3}$ to calculate the figure of merit (*zT*) at 300 K. *zT* values for holes are 0.5 and 0.6 along 'a' and 'c' respectively, whereas, for electrons, the values are 0.3 and 0.5 along 'a' and 'c' axis, respectively. Our calculated thermoelectric properties prompt us to predict that the holes as carriers would be a better choice for exploring the future thermoelectric applications in HgI₂.

4. Monolayer studies

4.1. Structural and electronic structure properties

These systems are layered and van der Waals solids which allows us to cleave the bulk systems into monolayers. The free-standing monolayers are created by giving a vacuum space of 15 Å along the 'z' axis. The structural stability of monolayers is confirmed through the calculated negative values of cohesive energies. The monolayer structure of HgI₂ is shown in Fig. 1(d). Fig. 6(a) displays the electronic properties of HgI₂ monolayer. This monolayer is a direct bandgap semiconductor with a bandgap of nearly 1.84 eV. To maintain the consistency with the bulk calculations, the Tb-mBJ functional is employed, showing the opposite trend compared to bulk HgI₂ as the bandgap decreases to 1.63 eV. The bands are flat along Γ -X in the valence band region, whereas they are more dispersive in the conduction band region. The semiconducting nature is also reflected in the DOS plots as shown in Fig. S5(a). Hg - d and I - p states are contributing most to the total DOS in the valence

band region, whereas Hg - *s* and I - *p* states are dominating in the conduction band region. HgBr₂ monolayer is shown in Fig. 1(e). This monolayer is also a direct bandgap semiconductor, as seen in Fig. 6(b). The bandgap is 2.43 eV which further improved up to 2.65 eV with the inclusion of TB-mBJ functional. The band profiles are almost identical along both Γ -X and Γ -Y in both valence band and conduction band region. Born effective charge tensors for monolayers are also computed, and the same is given in Table: S2. The Born effective charge for Hg and halide atom is not varying much when compared with bulk. The optical and thermoelectric properties are also explored to observe the effects of the electronic band structure and are discussed in the upcoming section.

4.2. Transport and optical properties

As a first step, we have calculated the mobility scaled by relaxation time (μ/τ) for the monolayers of HgI₂ and HgBr₂ to check the carrier transfer efficiency. The mobility scaled by relaxation time is shown in Fig. 7(a, b) for HgI2. As it is a tetragonal system in bulk, the properties must be the same along both the crystallographic axes, and the variation is observed only along $\ensuremath{\varGamma}\xspace{-X}$, and the value is almost the same as that of the bulk. The μ/τ of HgBr₂ is given in Fig. S6(a, b), and the same is calculated along both Γ -X and Γ -Y as the bulk HgBr₂ is orthorhombic and it is anisotropic, which decreases with temperature. The anisotropy for holes is not so pronounced, whereas it is appreciable for the electrons as the μ/τ along 'b' is nearly doubled compared to the value along 'a' axis. Next, the optical properties of monolayer HgI2 are calculated, which are given in Fig. S(7, 8). The real part of the dielectric constant is positive throughout the energy range. The absorption band edge is equal to the bandgap of this monolayer. The first transition is occurring beyond 2 eV, as seen from absorption spectra. The refractive index is constant up to nearly 2 eV, and its value is around 1.6, which is lesser than that obtained in bulk. The peaks observed in the reflectivity plot signify inter-band transition. Metallic character discussed in case of bulk when the real part of dielectric constant is negative, which is not seen here. The optical properties of the HgBr₂ monolayer are given in Fig. S(7, 8). The real part of dielectric spectra is constant up to photon energy equivalent to the bandgap. The transition is happening beyond 2 eV, as seen through peaks in both the real part of dielectric and absorption spectra. The anisotropy in the optical properties is seen here as the dielectric spectra along Γ -Y become negative between 4 to 6 eV, where the reflectivity is highest and shows metallic character.



Fig. 6. The band structure using Tb-mBJ functional for (a) HgI2, (b) HgBr2 monolayers.



Fig. 7. Mobility scaled by relaxation time of HgI2 monolayer (a) for holes (b) for electrons.

The value of the refractive index is nearly 1.3, which is quite lower than that of bulk. From the results, we found that these monolayers are less optically dense than bulk. Table 5 illustrates the static dielectric constant and static refractive indices for both the monolayers.

Subsequently, the thermoelectric properties are also calculated for both the monolayers. The thermopower for monolayer HgI₂ is given in Fig. 8(a, c). The magnitude of thermopower is decreasing with carrier concentration and increases with temperature. For HgI₂ monolayer, the values of thermopower are 670 μ V/K and 434 μ V/K for holes and electrons respectively at 300 K for carrier concentration of 10^{18} cm⁻³. Thermopower is isotropic for HgI₂ monolayer and shows the improvement over bulk. The electrical conductivity scaled by relaxation time (σ/τ) is also calculated and shown in Fig. S9(a, b). It is isotropic and almost temperature independent for both carriers. The power factor scaled by relaxation time which is the combined effect of both the thermopower and σ/τ , is also given in Fig. 8(b, d). The power factor for holes is temperature independent in low carrier concentration, whereas it is increasing with temperature for heavy hole concentration [Fig. 8(c)]. The power factor for electrons is increasing with temperature throughout the concentration range [Fig. 8(f)]. Similarly, we have calculated the thermopower for HgBr2 monolayer, and the values of thermopower are 586 μ V/K and 458 μ V/K for holes and electrons respectively at 300 K for carrier concentration of 10¹⁸ cm⁻³ [Fig. S10(a, d)]. The thermopower of holes is higher than that of electrons for both the monolayers. The σ/τ of HgBr₂ monolayer is shown in Fig. S10(b, e). A slight anisotropy is observed in σ/τ for both the carriers. The power factor scaled by relaxation time is anisotropic and increasing with temperature and its values are in the order of 10¹⁰ W/mK²s for both the carriers at 300 K in both HgI₂ and HgBr₂ monolayers [Figs. 8(b, d), S10(c, f)]. The improvement in the thermopower in monolayer HgI₂ over bulk together with the optical properties might fetch future low dimension device applications here.

Tabl	le	5

Dielectric constant	and refractive index of H	HgI ₂ and HgBr ₂ monolayers.
Compounds	Dielectric constant	Refractive index

Compounds	Dielectric c	olistalit	Reliactive index		
	xx	уу	n _{xx}	n _{yy}	
HgBr ₂	1.7	2.1	1.3	1.4	
HgI_2 (tetra)	1.6	-	2.5	-	

5. Conclusion

A systematic first-principles study of mercury-based halides has been done for both bulk and monolayer forms. The electronic band structure plots ensure the direct bandgap semiconducting nature here. The optical properties are anisotropic with birefringence values for HgCl₂ and HgBr₂ computed to be 0.27, whereas 0.06 for HgI₂ and are implying a wide range of applications in opto-electronic devices. The values of average lattice thermal conductivity are 0.27 W/mK, 0.23 W/mk, 0.09 W/mk at 300 K for HgI2, HgBr2 and HgCl2 respectively. The relaxation time and other thermoelectric properties are calculated for HgI₂ as it possesses the least bandgap among all the compounds. The mobilities of HgI₂ are consistent with the experimental values. The thermoelectric properties for the carriers are promising, but holes could be a primary choice with higher thermopower and figure of merit than that of electrons. The anisotropy observed in the bulk transport properties, and the van der Waals nature further motivated us to perform monolayer studies. Monolayer HgI2 and HgBr2 are also direct bandgap semiconductors and structurally stable. The thermoelectric properties could be the best choice for future applications in these monolayers as the thermopower for holes in HgI₂ monolayer is 670 μ V/K, whereas for bulk it was found to be 580 μ V/K at 300 K for carrier concentration of 10¹⁸ cm⁻³. Overall, our first-principles investigation predicts



Fig. 8. HgI2 monolayer: Thermopower (a, c) Power factor (b, d) as a function of concentration.

thermoelectric and opto-electronic applications in both the bulk and monolayer HgX_2 (X = Cl, Br and I).

CRediT authorship contribution statement

Sushree Sarita Sahoo: Executing the problem, Running the calculations, Data analysis, Manuscript preparation. Vineet Kumar Sharma: Running a part of the program, Running the calculations, Data analysis, Manuscript editing. Mayanak K. Gupta: Analysis of results, Editing the manuscript, Discussions. Ranjan Mittal: Analysis, Manuscript editing and validation of results. V. Kanchana: Problem Identification, Data analysis, Discussion of results, Manuscript preparation and editing, Supervision of work.

Declaration of competing 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.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.mtcomm.2021.102824.

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