A comparative study of structural, electronic and optical properties of cubic CsPbI₃: bulk and surface

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Abstract. In order to acquire a reasonable description of the structural, electronic and optical properties of the perovskite compound CsPbI₃, first principle calculations have been computed by density functional theory implemented in the WIEN2k code. The calculations are presented within PBE-sol for exchange correlation functions coupled with modified-Becke–Johnson (mBJ) exchange potential. The (001) surfaces of CsPbI₃ for varying thicknesses have been constructed using the StruCTeditor program implemented in the WIEN2k code. The lattice constant, band gap and DOS have been computed. The CsPbI₃ bulk and surface exhibit a direct band gap located at the *R* symmetry point of the Brillouin zone. The band gap approaches experimental values when the exchange correlation function is coupled with mBJ. The optical properties of CsPbI₃ were computed in terms of dielectric properties, refractive index, extinction coefficient, absorption coefficient, conductivity, reflectivity and energy loss. The direct band gap nature and high-absorption power of the surfaces of CsPbI₃ in the (001) direction in the infrared, visible and ultraviolet energy range make it suitable for use in optical and optoelectronic devices.

Keywords. CsPbI₃; surface; optical properties; electronic properties; mBJ potential.

1. Introduction

Globally, the demand for energy is increasing continuously from day to day. Diminishing fossil fuel reserves coupled with the concern about the environmental impact has necessitated the development of alternate energy conversion/storage systems which are environmentally friendly and also relatively cheap. One class of promising solid state solar cells with high efficiencies are the organic–inorganic lead perovskites which fulfil these demands [1–7]. Moreover, they are easily synthesized, are stable and make use of relatively cheap materials which have stimulated considerable research on these materials [8,9]. The family of perovskite crystals (ABX₃) show many interesting physical properties such as superconductivity, ferroelectricity, charge ordering, high-thermoelectric power, spin-dependent transport properties, colossal magneto-resistance and an interdependence of structural, magnetic and optical properties thereby having good potential as materials for optoelectronics [10,11]. Additionally, they also find use as catalytic electrodes in fuel cells, substrates and sensors.

Ternary CsPbI₃ semiconductors represent perovskite compounds which crystallize in the cubic structure with the space group *Pnma* with five atoms in the unit cell basis. In general, perovskite-based solar cells have a structure similar to CaTiO₃ with a general formula ABX₃. A and B are cations

of large sizes such as Rb, Cs, Pb, Sn and organic substances whereas X can be a halide (Cl, Br and I). It is well-known that the desired electrical and optical properties of solar cells for potential applications of this class of materials can be tailored by varying the type and amount of substitution into the lattice for any of the three species A, B and X [12,13]. These compounds have attracted tremendous attention in the last few decades because of their importance in light-emitting diodes, spintronic-based devices, energy storage devices and solar cell applications due to their good light absorbing properties [14–16].

Since practical applications often require such materials in the form of thin films, in the present study we have computed structural, electronic and optical properties of CsPbI₃ for both the bulk and (001) surface texture.

2. Computational details

In this study, the StruCTeditor program implemented in the WIEN2k code was used to create the surface structure of CsPbI₃ for (001) texture. The WIEN2k code has been used with full potential linearized augmented plane-wave (FP-LAPW) within the framework of density functional theory for the calculation of the structural, electronic and optical

properties of bulk and surface (001) CsPbI₃. Exchange correlations have been treated by using Perdew, Burke and Ernzerhof (PBEsol) generalized gradient approximation (GGA) and was corrected using a more advanced technique called modified-Becke–Johnson (mBJ) potential [17]. To avoid any charge leakage from the core, the value of the muffin tin sphere radius (R_{MT}) was chosen to be 2.5 a.u. for Cs, Pb and I. The plane-wave cut-off value was set to seven. The energy threshold was set to -6 Ry between the core and the valence states and Fourier expansion (G_{max}) was set to 12 (a.u.)⁻¹. The maximum value of angular momentum, l_{max} , was taken to be 10 for wave function expansion inside the atomic spheres. In the (001) direction of CsPbI₃, alternating sublayers of CsI and PbI₂ are present. CsI was considered for surface termination in order to avoid direct exposure of Pb at the surface. The (001) surface structures were spaced by 30 Å vacuum to avoid any interaction with the adjacent slab. Studies were performed for three different thicknesses, viz., 11.796 bohr, which is the distance between two Pb atoms, 23.592 and 47.184 bohr. For purposes of discussion, these are referred to as S1, S2 and S3 respectively in the rest of this paper. The calculations for the surface (001) were performed with 1 mRy force minimization, 0.00001e electron charge and 0.00001 Ry energy as criteria for self-consistent force convergence.

3. Results and discussion

3.1 Structural properties

The structural parameters of bulk CsPbI₃ have been calculated by determining the unit cell energy as a function of the unit cell volume using the Murnaghan's equation of state [18] which is as follows:

$$E(V) = E_0 + BV_0 \left[\frac{1}{B_p(B_p - 1)} \left(\frac{V^{1+B_p}}{V_0} \right) + \frac{1}{B_p} \frac{V}{V_0} - \frac{1}{B_p - 1} \right]. \quad (1)$$

In the above equation, E_0 is the minimum ground state energy at $T = 0$ K, B is the bulk modulus, B_p is the pressure derivative of the bulk modulus and V_0 is the equilibrium volume.

The optimization of volume of a unit cell of CsPbI₃ was performed to obtain the structural properties such as lattice constant, a (Å), bulk modulus, B (GPa), pressure derivative, B_p and ground state energy, E_0 . The optimization curve for CsPbI₃ is shown in figure 1. The values obtained for a , B , B_p and E_0 are 6.24 Å, 17.82 GPa, 4.665 GPa and 100117.329 Ry, respectively. The value of the optimized lattice parameter (6.24 Å) was used for surface analysis.

Bulk CsPbI₃ has a cubic structure with the $Pm\bar{3}m$ space group. The unit cell consists of five atoms with Pb and Cs occupying positions (0, 0, 0), (1/2, 1/2, 1/2), respectively. I

Figure 1. Optimization curve of bulk CsPbI₃.

occupies (0, 1/2, 0), (1/2, 0, 0) and (0, 0, 1/2) sites. The (001) surface of CsPbI₃ has a tetragonal structure. The unit cells of S1, S2 and S3 consist of four (1 Pb, 1 Cs, 2 I), eight (2 Pb, 2 Cs, 4 I) and sixteen (4 Pb, 4 Cs, 8 I) atoms, respectively. The crystal and surface structure of CsPbI₃ for all three surface samples and the bulk are shown in figure 2. The lattice parameters, space group and volume are listed in table 1.

3.2 Electronic properties

The electronic properties of CsPbI₃ can be well explained in terms of the band structure and density of states (DOS). In the band structure diagram, energy vs. k vector of the first Brillouin zone is plotted as shown in figure 3. From these curves, we can ascribe the electronic nature of the material in terms of whether the crystal is metallic or non-metallic, existence of an energy gap, the energy gap being direct or indirect, etc. In CsPbI₃, both the valence band (VB) maximum and the conduction band (CB) minimum lie on the R and M points, which indicate that it has a direct band gap. The band gap calculated for the bulk CsPbI₃, S1, S2, S3 are 1.55, 1.95, 1.74 and 1.36 eV respectively along the R point and 2.47, 1.95, 1.74 and 1.36 eV along the M point (table 2). The variation of the band gap and volume of the unit cell with the thickness of the surface structures are presented in figure 4a and b. A linear decrease in the band gap and an increase in the volume of the (surface) unit cell are observed as the thickness of the slabs is increased from 12 to ~48 bohr. Correspondingly, the band gap decreases linearly as the volume of the surface increases (figure 4c). This is because with an increase in the volume due to an increase in the lattice constant(s), the overlap of the wave functions of the valence and core electrons also decreases, thereby weakening the bonding of valence electrons. Thus, the minimum energy required to free electrons into the CB becomes correspondingly lesser which is reflected in the narrowing of the band gap as observed. Moreover, a shift in the VB above the Fermi level is observed for S3, i.e., the one with a thickness of 47.184 bohr, pointing to

Figure 2. The (001) surface structure of CsPbI₃ with varying thicknesses: (a) S1, (b) S2, (c) S3 and (d) bulk structure.

Table 1. Lattice constant, space group and band gap of bulk and (001) surface CsPbI₃.

Sample name	Lattice constant (<i>a</i>), Å	Lattice constant (<i>c</i>), Å	Space group	Volume, atomic unit
Bulk CsPbI ₃	6.24	6.24	<i>Pm3m</i>	1641.29
S1	6.52	22.39	<i>P4mm</i>	6429.60
S2	6.52	28.92	<i>P4mm</i>	8304.78
S3	6.24	40.81	<i>P1L1</i>	10,734.22

a shift from semiconducting to metallic nature on increase in the thickness of the slab.

Figure 5 shows the total and partial DOS for CsPbI₃ bulk and surfaces. It is seen that for both surface and bulk, below the Fermi energy level, i.e., for the VB, the p state of the I atom and the s state of the Pb atom contribute whereas above the Fermi energy, i.e., in the CB, Pb p and Cs d state contributions are observed.

3.3 Optical properties

For renewable-energy production focussing on the efficiency of solar energy-based novel devices, the optical parameters are of utmost importance. The interaction of electromagnetic

Figure 3. Electronic band structures of (a) bulk CsPbI₃, (b) S1, (c) S2 and (d) S3.

radiation with matter is a function of the energy of the radiation and the optical properties of the material can therefore be characterized in terms of constants of the material such as electrical conductivity, dielectric constant, refractive index, etc. These constants are, therefore, functions of the frequency of the radiation of which the dielectric function is one of the most important. It is described as a complex function of the form $\varepsilon = \varepsilon_1 + i\varepsilon_2$, obtained by the use of the Kramers–Kronig relation [19] and is used to describe the optical properties of solids. The Kramers–Kronig relation is as follows:

$$\text{Re } \varepsilon(\omega) = \delta + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \text{Im } \varepsilon(\omega')}{\omega' - \omega^2} d\omega'. \quad (2)$$

In this equation, P is the momentum component, ω represents the complex angular frequency and $\varepsilon(\omega')$ represents the dielectric constant.

All other optical constants such as refractive index $n(\omega)$, extinction coefficient $k(\omega)$, reflection $R(\omega)$, absorption $\alpha(\omega)$, conductivity $\sigma(\omega)$ and energy loss function $L(\omega)$ can be derived from the real and imaginary parts of the dielectric function. These constants are computed by using the following equations [20]:

$$n(\omega) = \sqrt{\frac{|\varepsilon(\omega)| + \text{Re } \varepsilon(\omega)}{2}}, \quad (3)$$

$$k(\omega) = \sqrt{\frac{|\varepsilon(\omega)| - \text{Re } \varepsilon(\omega)}{2}}, \quad (4)$$

$$R(\omega) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \quad (5)$$

Table 2. Band gaps of the CsPbI₃ bulk and (001) surface at different symmetry points.

Sample name	$E_g^{\text{R-R}}$, eV	$E_g^{\text{M-M}}$, eV
Bulk CsPbI ₃	1.55	2.47
S1	1.95	1.95
S2	1.74	1.74
S3	1.36	1.36

$$\alpha(\omega) = \frac{4\pi k(\omega)}{\lambda}, \quad (6)$$

$$\sigma(\omega) = \frac{2W_{cv}h\omega}{2\pi E_0^2}, \quad (7)$$

$$L(\omega) = -\text{Im} \left(\frac{1}{\varepsilon_1(\omega)} \right). \quad (8)$$

Here, λ represents the wavelength, W_{cv} the transition probability per unit time, h the Planck constant and E_0 the ground state energy.

For use in various optoelectronic devices, it is necessary to explore the optical properties. The results for the real part of dielectric function ($\varepsilon_1(\omega)$), imaginary part of dielectric constant ($\varepsilon_2(\omega)$), refractive index ($n(\omega)$), optical conductivity ($\sigma(\omega)$), extinction coefficient ($k(\omega)$), absorption coefficient ($I(\omega)$), reflectivity ($R(\omega)$), energy loss function ($L(\omega)$) as function of photon energy for CsPbI₃ bulk and surfaces with various thicknesses are shown in figures 6 and 7.

In figure 6a, the real part of the dielectric function for CsPbI₃ is plotted. In the plot, the zero frequency limit $\varepsilon_1(0)$ is an important quantity which describes the electronic polarizability and using its square root, according to the relation $n(0) = \sqrt{\text{Re } \varepsilon(0)}$, one can calculate the static refractive index [21]. From the plot it can be seen that zero frequency limit $\varepsilon_1(0)$ is the highest for the bulk CsPbI₃ and as the thickness of the CsPbI₃ surface is increased, $\varepsilon_1(0)$ increases along both the crystallographic axes. From figure 8a, we can infer that the slope is steeper for $E \parallel z$ i.e., the change in the static dielectric constant is faster when the component of the electric field is parallel to the z -axis as compared to the x/y -axis. The values of $\varepsilon_1(0)$ and $\varepsilon_1(\text{max})$ calculated for bulk CsPbI₃, S1, S2, and S3 are presented in table 3. For both bulk and surfaces, $\varepsilon_1(\omega)$ is observed to first increase, reach a maximum and then decrease (figure 6a). However, for bulk CsPbI₃, $\varepsilon_1(\omega)$ at 9 eV falls below zero, i.e., it has a negative value implying that at this energy, the wave does not propagate inside the matter or that the wave is attenuated, whereas this attenuation is not observed for the surfaces. Reflectivity is defined as the fraction of light reflected at an interface and

Figure 4. Surface slab variation of: (a) thickness with bandgap, (b) thickness with volume and (c) volume with bandgap. Lines represent linear fit to the points.

Figure 5. Total and partial DOS of CsPbI₃: (a) bulk, (b) S1, (c) S2 and (d) S3.

Figure 6. Calculated optical parameters: (a) real part of the dielectric function, (b) reflectivity, (c) refractive index and (d) energy loss function.

is generally high for metals due to their opacity, whereas it is low for transparent materials. Figure 6b shows reflectivity coefficient $R(\omega)$ of the samples. The variation of $R(0)$ with increasing thickness is presented in figure 8b and shows a trend similar to $\varepsilon_1(0)$. It can be seen that $R(0)$ increases as the slab thickness is increased and is in agreement with the results obtained from DOS. Values of the zero-frequency reflectivity and the maximum reflectivity are given in table 3. The maximum reflectivity value is about 33% at 11.2 eV for bulk CsPbI₃. A strong reflectivity maximum between 2.6 and 12 eV arises due to interband

transitions. Also, it is clear from the plot that reflectivity is maximum at the point at which $\varepsilon_1(\omega)$ becomes negative and the material exhibits a metallic nature for the negative value of $\varepsilon_1(\omega)$. Reflectivity is usually high in the UV–visible–infrared range of radiation for metals making them opaque and thus not allowing radiation of these wavelengths to transmit through them.

When light photons get transmitted through a material, it causes polarization of electrons and results in the reduction of speed. The refractive index is used to describe the relative velocity when radiation passes through a medium and is an important parameter to describe the absorption of light. Figure 6c shows the refractive index of bulk CsPbI₃ and surface slabs. The $n(0)$ and maximum refractive index $n_{\max}$ are given in table 3. It is seen that $n(0)$ increases as the thickness of the CsPbI₃ surface is increased and is 2.19 for the bulk compound (figure 8c). The trend of the refractive index is also similar to that of $\varepsilon_1(\omega)$, i.e., the refractive index first increases, reaches a maximum value, then starts decreasing and further goes below unity in some energy ranges indicating a negative domain shift in group velocity. This leads to the conversion of the medium from linear to non-linear making the material superluminal [22]. The energy loss function (figure 6d) describes the energy loss of a speedily moving electron travelling through the material and one can obtain the plasmon frequency from the peaks of this diagram. The imaginary part of the dielectric constant, plotted in figure 7a, gives information about the absorption of free electrons or the absorption behaviour of CsPbI₃. It can be seen that the edge of $\varepsilon_2(\omega)$, i.e., the threshold energy, starts at 1.5, 1.83, 1.72 and 1.38 eV for bulk, S1, S2 and S3, respectively and is closely related to their band gap. It can be seen that the intensity of the absorption peaks is sharper as the thickness

Figure 7. Calculated optical parameters: (a) imaginary part of the dielectric function, (b) extinction coefficient, (c) absorption and (d) optical conductivity.

Figure 8. Variation of optical parameters as a function of thickness for (001) surface CsPbI₃: (a) zero frequency limit of dielectric constant, (b) zero frequency limit of reflectivity coefficient and (c) zero frequency limit of the refractive index. Lines are linear fit to points.

of the surface CsPbI₃ is increased. This can be attributed to the narrowing width of the VB. Various peaks are generally observed for lead halide perovskite compounds and arise because of the inter-band or intra-band transitions and the corresponding transition can be identified from the DOS. For bulk CsPbI₃, three peaks are visible at 3.37, 7.11 and 8.88 eV (figure 7a). The peak at 3.37 eV is due to the transition of the electron from the I p state of the VB to the Pb p state in the CB. The peak at 7.11 eV arises due to the transition from the I p state to the Pb d state in the CB. The 8.88 eV peak owes its origin to the transition from the Cs p state to the Pb p state. Similar trends and transitions are observed for the surfaces as well. The extinction coefficient describes the loss of energy due to absorption as it moves through an optical medium. Figure 7b shows the plot for extinction coefficients of bulk and surfaces. A low value of $k(\omega)$ implies that the wave has simply passed through, whereas a high value denotes that considerable absorption has taken place. It can be clearly seen from the graph that there are various minima and maxima at different energies. The absorption coefficient presented in figure 7c shows absorption in the range of 2–14 eV. The optimal absorption of bulk and surface CsPbI₃ occurs in the ultraviolet and visible ranges indicating its usefulness and applications for various photonic and optoelectronic devices. Figure 7d shows the plot of the optical conductivity, $\sigma(\omega)$. It is clear from this plot that the optical conductance initiates at around 1.58 eV for bulk CsPbI₃ and has features similar to that of the absorption coefficient $I(\omega)$ seen in figure 7c.

4. Conclusion

The aim of this work is to study the variations in the structural, electronic and optical properties of CsPbI₃ in the bulk and (001) surface structures and have been investigated by means of the FP-LAPW method in the WIEN2k code within GGA for exchange correlation functions. It is seen that the surface growth of CsPbI₃ in the (001) direction changes the crystal structure from cubic to tetragonal. The present study suggests that the band gap of CsPbI₃ surfaces can be controlled by controlling the thickness of the slabs since a systematic decrease in the band gap is observed with an increase in the thickness.

Table 3. Zero and maximum frequency limit of $\epsilon_1(\omega)$, $R(\omega)$ and $n(\omega)$.

Parameters	CsPbI ₃	S1		S2		S3	
		$E \parallel x$	$E \parallel z$	$E \parallel x$	$E \parallel z$	$E \parallel x$	$E \parallel z$
$\epsilon_1(0)$	4.797	2.410	1.775	3.072	2.538	3.759	3.734
$\epsilon_1(\max)$	7.212	3.710	2.618	4.950	3.855	5.750	5.190
$R(0)$	0.139	0.046	0.020	0.074	0.053	0.102	0.102
$R(\max)$	0.330	0.180	0.120	0.220	0.130	0.220	0.200
$n(0)$	2.190	1.553	1.334	1.742	1.596	1.933	1.933
$n(\max)$	2.752	1.980	1.650	2.280	1.980	2.450	2.320

The optical properties of the surfaces of CsPbI₃ in the (001) direction are good in the visible and ultraviolet region and hence is a highly promising material for use in photonics and optoelectronic devices.

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