First-principles calculations of electronic and optical properties in the bulk and on the (001) surface of CsPbCl₃

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Abstract. We perform density functional theory using first-principles calculations in order to investigate the band structure, density of states, the real and imaginary part of dielectric function, refractive index and optical absorption of CsPbCl₃ in the bulk and (001) surface structure. Energy bands exhibits wide and direct bandgap. When CsPbCl₃ is extended to (001) surface a decrease of band gap is observed with increasing thickness. The optical constants observed exhibits optimal properties in the ultraviolet and visible range indicating its usefulness in photonic, optoelectronic, photovoltaic and optomagnetic devices.

1. Introduction
Perovskite which have general formula AMX₃ where, A and M can be cations like Pb, Cs, Sn, Rb, organic material viz. CH₃NH₃, CH₃CH₂NH₂ and X be a halide, possess unique properties like strong light absorption, high charge carrier mobility, long carrier diffusion lengths and small exciton binding energies and hence are promising materials for use in optoelectronic, photo detectors and photonic devices [1-7]. Moreover, they exhibit physical properties like colossal magneto- resistance, spin dependent transport properties, superconductivity, high thermoelectric power, ferroelectricity and charge ordering [8-10]. The practical applications of perovskites in optoelectronics often require such materials to be in the form of thin films, hence its surface study would assist in analyzing the electronic and optical properties.

In our present work using the first principles approach of the density functional theory (DFT) as in WIEN2k code, we have analyzed the structural, electronic and optical properties of bulk CsPbCl₃ as well as its (001) surface texture.

2. Computational detail
To perform the full potential linearized augmented plane wave (FP-LAPW) method of the density functional theory, we have used WIEN2k software package by Peter and Blaha [11] for the calculation of structural, electronic and optical properties of CsPbCl₃ bulk and its 001 surface. Our calculations was performed using exchange correlations treated by using Perdew, Burke, and Ernzerhof (PBE-sol) generalized gradient approximation (GGA) and was corrected using a more advanced technique called modified Becke Johnson (mBJ) potential [12]. Using PBE-sol exchange correlations, we optimized the lattice constants and atomic positions of unit cell of bulk CsPbCl₃. The muffin tin sphere radius (Rₘᵣ) value was chosen to be 2.5a.u for Cs, Pb and Cl. The plane-wave cut off value, energy threshold, Fourier expansion (Gₘₐₓ), angular momentum, energy convergence and charge convergence was set to
7, −6.0 Ry, 12 (a.u.)\(^1\), 10, 0.0001 Ry and 0.0001e respectively. Also, CsPbCl\(_3\) (001) surface with different thickness were modelled with 2D slabs using Structeditor program implemented in WIEN2k code. Surface terminated by CsX was considered in order to avoid direct exposure of Pb at the surface alongwith spacing of 30Å vacuum. Studies were done by creating surface with different thickness which was taken to be the distance between 2 Pb atoms and their multiples. The thicknesses used for this purpose were 10.628 bohr, 21.256 bohr and are refered to as S1 and S2 in the rest of the paper.

3. Results and Discussion

3.1. Structural Properties

The volume of unit cell of CsPbCl\(_3\) is optimized to obtain structural properties like lattice constant \(a(A^\circ)\), ground state energy \(E_0\), bulk modulus \(B(GPa)\) and pressure derivative \(B_p\). The optimization curve is given in figure 1(a). The calculated parameters are presented in table 1. For performing the surface study, we have used the optimised lattice parameter. The cubic unit cell of bulk CsPbCl\(_3\) comprise of 5 atoms having spacegroup Pm-3m and occupying atomic positions as follows: Cs occupies (½, ½, ½) site, Pb occupies (0, 0, 0) site and Cl occupies (0, ½, 0), (½, 0, 0), (0, 0, ½) sites. The (001) surface of CsPbCl\(_3\) has tetragonal structure. The crystal and surface structure (001 orientation) of CsPbCl\(_3\) are shown in figure 1(b) and their lattice parameters, space group and volume are listed in table 1.

![Figure 1](image-url)
Table 1. Structural parameters of bulk and (001) surface CsPbCl$_3$.

| Sample Name | Lattice parameter (Å) | Volume (Å$^3$) | Spacegroup | Ground state energy E (Ry) | Bulk modulus B (GPa) | Pressure derivative B$_p$ (GPa) |
|-------------|-----------------------|----------------|------------|---------------------------|---------------------|--------------------------------|
| CsPbCl$_3$  | a=5.62, c=5.62        | 177.50         | Pm-3m      | 60185.852                 | 25.45               | 4.5477                         |
| S1          | a=5.62, c=21.49       | 678.75         | P4mm       | -                         | -                   | -                              |
| S2          | a=5.62, c=27.11       | 856.25         | P4mm       | -                         | -                   | -                              |

3.2. Electronic Properties

Figure 2 shows the band structure diagram. The electronic band gap is described by difference between the states at the conduction band minimum (CBM) and valence band maximum (VBM). From the figure it can be seen that in CsPbCl$_3$ bulk and (001) surface, the conduction band minimum and valence band maximum, both are located at the $R$ symmetry point, hence these perovskite compounds are direct band gap materials. Direct band gaps are also observed at other symmetry points ($\Gamma$, $X$, $M$) in this compound (table 2).

The electron distribution probability in energy spectrum can be described by density of states (DOS). The total DOS, using mbj-GGA approximation for bulk and (001) surfaces of CsPbCl$_3$ are shown in figure 3. On comparison with the bulk and (001) surface of CsPbCl$_3$ it is seen that there is slight shifting of the upper valence bands towards the Fermi level for the surface structures. The DOS for all the 3 structures can be bifurcated in 2 regions; the valence band (VB) region in the range of -4.1 eV to -0.2 eV and the conduction band region. For both surface and bulk CsPbCl$_3$, in VB region contribution is majorly from Pb-6s, Pb-d and Cl-p orbitals and in conduction band the contributions are majorly from Pb-p state, Cs-d state [13].

Table 2. Band gaps of CPbCl$_3$ bulk and (001) surface at different symmetry points.

| Sample name   | $E_{g}^{R-R}$ (eV) | $E_{g}^{M-M}$ (eV) | Experimental band gap (eV) |
|---------------|--------------------|--------------------|----------------------------|
| CsPbCl$_3$ bulk | 2.85               | 4.16               | 3.01 [14]                  |
| CsPbCl$_3$ S1 | 2.83               | 2.83               | -                          |
| CsPbCl$_3$ S2 | 2.40               | 2.40               | -                          |
Figure 2. Band structure of (a) bulk CsPbCl$_3$ (b) S1 CsPbCl$_3$ (c) S2 CsPbCl$_3$.

Figure 3. Total density of states of (a) CsPbCl$_3$ bulk (b) S1 and (c) S2.
3.3. Optical Properties

Study of optical properties play a significant role in materials which are been used for optoelectronics, photonics, photovoltaic applications, etc. The optical parameters of the solids can be calculated by frequency dependent dielectric function \( \varepsilon(\omega) \) obtained through Kramers-Kronig relation \[15\].

Figure 4(a) exhibits the real part of dielectric function \( \varepsilon_1(\omega) \) and can be seen that the zero frequency limit \( \varepsilon_1(0) \) is highest for bulk CsPbCl\(_3\) and with increasing thickness, \( \varepsilon_1(0) \) increases. It can be observed that \( \varepsilon_1(\omega) \) firstly increases and reaches a maximum value and then goes on decreasing. In bulk CsPbCl\(_3\) the wave is attenuated at higher energies i.e. 12.31 eV since \( \varepsilon_1(\omega) \) becomes negative \[16\]. Attenuation is not observed for surfaces. The imaginary part of the dielectric constant (figure 4(b)) gives information about the absorption behaviour of free electrons and has a direct relation with the band gap of the material. Comparing the CsPbCl\(_3\) bulk and (001) surface, it is observed that the edge of \( \varepsilon_2(\omega) \) starts at 2.84 eV, 2.70 eV and 2.38 eV related to their band gap of 2.85 eV, 2.83 eV and 2.40 eV for bulk CsPbCl\(_3\), (001) S1 CsPbCl\(_3\) and (001) S2 CsPbCl\(_3\) respectively. Various peaks are observed for CsPbCl\(_3\) and are attributed to inter-band or intra band transitions. Identification of these peaks transition can be done analyzing density of states. For CsPbCl\(_3\), 4 peaks at 4.55 eV, 6.43 eV, 9.45 eV and 12.17 eV are observed. The maximum refractive index \( n_{\text{max}} \) and static refractive index \( n(0) \) are tabulated in table 3. The spectrum of \( n(\omega) \) is similar to \( \varepsilon_1(\omega) \). It first increases to reach a maximum and then decreases. It is clear from the figure that as the thickness of CsPbCl\(_3\) surface is increased the static refractive index also increases. The extinction coefficient presented in figure 4(d) for CsPbCl\(_3\) bulk and surface refers to the amount of attenuation caused when light propagates through the material. High value of \( k(\omega) \) implies that absorption of light has taken place whereas a low value denotes light passing out from material without much loss. From the graph it is observed that value of \( k(\omega) \) is low. The calculated optical parameter like absorption coefficient of CsPbCl\(_3\) bulk and surface compounds relates the response of these materials to the incoming photons. The plot is shown in figure 4(e) and for CsPbCl\(_3\) bulk along with their surface structures shows absorption in the range of 2-14 eV. The absorption coefficient for surface films has smaller value than their bulk compound. Optimal absorption is observed in the visible and ultraviolet range which makes these compounds suitable for photonic and optoelectronic devices like LED, solar cell etc. Also, many peaks are observed at different energies or wavelength showing the absorption of maximum light at different wavelengths. This property of the material can be used for wavelength filtering purpose in those regions.

| Parameters | CsPbCl\(_3\) bulk | CsPbCl\(_3\) S1 | CsPbCl\(_3\) S2 |
|------------|--------------------|----------------|----------------|
| \( \varepsilon(0) \) | 2.70 | 1.71 | 2.15 |
| \( \varepsilon(\text{max}) \) | 3.89 | 2.43 | 2.92 |
| \( n(0) \) | 1.64 | 1.31 | 1.47 |
| \( n(\text{max}) \) | 2.02 | 1.55 | 1.73 |
Figure 4. optical constants (a) real part of dielectric function $\varepsilon_1(\omega)$, (b) imaginary part of dielectric function $\varepsilon_2(\omega)$, (c) refractive index $n(\omega)$, (d) extinction coefficient $k(\omega)$, and (e) absorption coefficient $\alpha(\omega)$. 
4. Conclusion
This work aims at studying the variations in the electronic, structural and optical properties of CsPbCl$_3$ in the bulk and (001) surface structures by means of the FP-LAPW method in the WIEN2k code using modified Becke Johnson potential for exchange correlation functions. Bandstructure indicates that bulk and (001) surface of CsPbCl$_3$ has a wide and direct bandgap located at R symmetry point. Moreover, surface study is suggestive of fabricating thin films with minimum thickness, which also retains effective optical behaviour as compared with the bulk. From the study of optical properties and direct band gap nature of the compounds we can conclude that both, bulk and (001) CsPbCl$_3$ are suitable for photonic, photovoltaic and optoelectronic devices.

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