Opto-Electronic Properties of Methyl-Ammonium Lead Halide: A First Principle Approach

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Abstract. Using first principle approach, based on Density functional theory (DFT), we have investigated the ground state opto-electronic properties of methyl-ammonium lead halide (MLH), CH₃NH₃PbX₃ where (X=Cl, Br, I), the key materials for opto-electronic applications, especially for efficient and low cost solar cell. The halide contents are important in electronic and optical behavior such as band structure, density of states, absorption, optical conductivity etc. The nature of calculated band structure (BS) and density of states (DOS) clarify that these are semiconductor. Further-more CH₃NH₃PbPbI₃ has effective band gape and can be utilized in opto-electronic applications especially in solar cell.

1. Introduction
Recently, Organic-inorganic compounds termed as hybrid perovskites and elemental name methyl-ammonium lead halide has attracted researchers of photovoltaic community since this material had presented outstanding power conversion efficiencies [1]. These outstanding results of MLH astonished scientific community in very short time, so they are compelled towards these economical material regions for upcoming low cost solar cells. Methyl-ammonium lead halide (MLH) shows inspiring role in photovoltaic devices with its good band-gap, high extinction coefficient [2] as well as high charge carrier mobility [3]. The absorption range of MLH compounds are from visible to infrared, so its uses in opto-electronic industry is beyond doubt [4]. Recently 23.7% certified efficiency is recorded and can be seen in National Renewable Energy Laboratory (NREL) website [5]. The MLH general chemical formula is taken as AMX₃. The “A” represent organic part (CH₃NH₃) while “M” and X represent (Pb) and (Cl, Br, I) respectively. The MLH has same structure as traditional perovskite discovered in 1839, so it is also known as hybrid perovskite [6]. The MLH has: (i) high diffusion length, (ii) good electron and hole transportation due to low exciton energy and (iii) strong optical absorption [7, 8]. MLH film can be made by heat combining with mesoporous film and spin coating method [9].

Due to instability in MLH structure the research on its mechanical strength is so fast in recent years and until now [10]. Now for commercialization of MLH we need stability as well, there is a strong boundary for spreading this technology outside from laboratory because of environmental influence [11]. In this research, we investigated opto-electronic properties of Methyl-ammonium lead halide AMX₃ (A=CH₃NH₃, M=Pb, X=Cl, Br, I) with first principle approach. The ground state electronic properties comprehensively described by Band structure and density of states while optical properties is discussed using absorption co-efficient, Optical conductivity, reflectivity and dielectric constant.
2. Method of Calculation

In this work we used Wien2K software based on density functional theory. The GGA (Generalized Gradient Approximation) was used which is upgraded version of LDA (Local Density Approximation) for structure optimization [12-15]. The lattice constants were optimized and relaxed atomic positions till forces converged to \((5 \times 10^{-3} \text{ eV/A}^0)\) and energy converged to \(10^{-4} \text{ eV}\). The calculations are taken from (FP-LAPW) method based on wien2k programming software.

All the three compounds are simple cubic; we make a super cell of \((2 \times 2 \times 1)\) which is shown in optimized structure in figure 1(b). Also we set \(k\) points 500 and the path taken for Brillouin zone is \((\Gamma \text{ R X M } \Gamma)\), there lattice constants are \(5.679 \text{ A}^0\), \(5.920 \text{ A}^0\) and \(6.329 \text{ A}^0\) for AMCl\(_3\), AMBr\(_3\) and AMI\(_3\) respectively.

Every single atom consists of two muffin-tin sphere, and that space area has two regions which is non-overlapping spheres interior and interstitial region. For this calculation We have taken muffin-tin sphere in Bohr radius of \(2.5 \text{ a}_0, 1.31 \text{ a}_0, 1.27 \text{ a}_0\), and \(0.68 \text{ a}_0\) for Pb-Cl-Br-I, C, N and H respectively. We have set our smallest muffin-tin radius \(R_{\text{mt}} \text{K}_{\text{max}}\) to 7 and \(G_{\text{max}}\) to 20 for all three compounds.

3. Results and Discussion

The Methyl-ammonium lead halide (MLH) compounds exhibit cubic structure and showed semiconductor nature. After optimization we relaxed the atomic position of structure, which shows good agreement with previous and experimental and theoretical findings [16]. The figure 1 shows the structure of AMX\(_3\) without and with optimization.

The band structures (BS) and density (DOS) of states plots are drafted for the investigation of electronic nature and absorption coefficient, optical conductivity, refraction, reflection and dielectric constant are concisely discussed with plots for the optical nature of MLH using GGA scheme.

![Figure 1. Structural optimization of AMX\(_3\) (Pb at center, sides (Cl, Br, I) and corners CH\(_3\)NH\(_3\))](image-url)

3.1. Band Structure

We have investigated BS information for all MLH compounds which is shown in figure 2. In this theoretical work the band structure is calculated for AMX\(_3\) using GGA scheme. Band structure information for AMX\(_3\) is carried out using GGA approximation, which is shown in figure 2(a), (b) and (c). Band structure calculations shows that all the three compounds are semiconductor in nature with band gap \(1.98 \text{ eV}, 2.78 \text{ eV}\) and \(2.36 \text{ eV}\) for AMI\(_3\), AMCl\(_3\) and AMBr\(_3\) respectively.
Figure 2(a) shows the band structure of AMCl$_3$. The path taken for cubic structure is Γ, R, X, M, Γ. The band structure of AMCl$_3$ indicates that, it is semi-conductor material with indirect band gap for VBM and CBM don’t lie at same point of crystal momentum, as revealed in figure 2(a). The CBM occurs at 2.92 eV above Fermi level while VBM exist below Fermi level at 0.12eV. The Cl-p$_x$ and Cl-p$_y$ states contributed in VBM while Pb-p$_x$, Pb-p$_y$ and Pb-p$_z$ states contributed in CBM. The compound AMBr$_3$ has also shown indirect band gap. The figure 2(b) shows that CBM occurs above Fermi level at 2.50eV while VBM occurs below Fermi level at 0.004eV. The AMI$_3$ band structure shows it is direct band gap nature shown in figure 2(c). Its band gap occurs at point M in Brillion zone. The CBM lies above Fermi level at 1.90eV while VBM lies below Fermi level at 0.02 eV. The CBM is consist of I-p$_x$, I-p$_y$ and Pb-p$_x$ states and VBM Pb-p$_x$, I-p$_x$ and I-p$_y$ states. In all three compounds halide content is dominant at valance band and Lead is dominant at conduction band. Strong optical transition is possible because of large contribution of Valance band energy states conduction band; hence it opens the importance of MLH in opto-electronic applications.

![Figure 2. Calculated band structure of AMX$_3$](image)

3.2. Density of States
Density of states information is very useful in explaining the band structure of material. The density of states as total density (TDOS) and partial density of states (PDOS) was plotted and showed in figure 3.

Looking towards all three compounds, it is clear that the contribution to the valence and corners at right and conduction band corners left is atom Pb p-orbital and atoms Cl, Br, I p-orbital. For partial density of states AMCl$_3$, p$_x$ and p$_y$ orbitals of p-block Cl atom and p$_z$ orbital of Pb is seen dominant contribution at valance band edge while we have found the minor contribution of Cl atom p$_x$ and p$_y$ states. The halide and lead participation in CB and VB is due to good bond length between these two contents.

The compound AMBr$_3$ valance band consist atom p-block Br atom p$_x$, p$_y$ dominant contribution and minor contribution of p-block Pb atom p$_z$ orbital. The conduction band of AMBr$_3$ is combination of of p-block Pb atom p$_x$ and p$_y$ orbitals and Br atom p$_x$ orbital while Br atom p$_y$ orbital contribution is less at conduction band.

For AMI$_3$ valance band contribution is due to p-block I atom I-p$_x$, I-p$_y$ and I-p$_z$ orbitals and minor contribution of Pb atom Pb-p$_x$, Pb-p$_y$ and Pb-p$_z$ orbitals. For the conduction band it is found to be maximum participation of p-block Pb atom orbitals and minimum participation of p-block I atom orbitals.
Figure 3. Total and partial density of states of AMX$_3$

3.3. Optical Properties
In this work we calculated the optical properties of MLH AMX$_3$ by using GGA approximation. These optical properties include dielectric constant, refractive index, reflectivity, absorption coefficient and optical conductivity. The Optical properties of MLH shows exceptional results that’s why researchers are attracted towards this material for near-future commercialization.

The absorption coefficient determines how much penetration occurs of certain wavelength of light before it absorbed. Light is poorly absorbed in Material with low absorption coefficient and if material is thin enough then it becomes transparent to that specific wavelength. The absorption lines in figure 4(a) represent different compounds absorption in specific energy from (0-10eV) and shows that green line AMI$_3$ has good absorption coefficient in desirable energy regime so it can absorb light as much than others. All other compounds showed good properties, the red line represent AMBr$_3$ and black represent AMCl$_3$ with distinctive behaviours due to halide contents.
Figure 4. Optical properties of AMX₃.

The optical conductivity of MLH described the behaviour of these Materials in the presence of energy (eV). Within the visible energy range (1.63 to 3.26 eV) the compound AMI₃ (green) shows
outstanding optical conductivity in figure 4(b). The AMCl$_3$ and AMBr$_3$ also show the dominant properties but less than AMI$_3$ due to larger band gape. Figure 4(c) and (d) show real and imaginary parts of refraction, green line represents AMI$_3$, red line represents AMBr$_3$ and black line represents AMCl$_3$. In figure 4(e), the real part of dielectric constant behaviour of material is discussed, the dielectric property is decreases with increase in energy electric field, looking at the green, red and black lines it is clear that sudden down shift occurs when energy is increased. Hence they are good semiconductors and conduct current. Figure 4(f) shows imaginary part of dielectric constant (dielectric loss) of MLHs. The property which reflects electromagnetic radiations from surface of material is known as reflectivity of material. It is very useful in seeing of objects colour and can be used in many purposes, reflective material in darkness when source of light is available e.g road signs etc. Figure 4(g) shows reflectivity of MLH compounds in specific energy range and shows very good results.

4. Conclusion

The opto-electronic properties of AMX$_3$ where (A=CH$_3$NH$_3$, M=Pb, X=Cl, Br, I) is collectively calculated by using density functional theory (DFT) with Generalized Gradient approximation (GGA) approximation. From band structure calculations the band gapes are 2.78 eV, 2.36 eV and 1.98 eV for AMCl$_3$, AMBr$_3$ and AMI$_3$ respectively. All the compounds are found to be semi-conductor in nature, The AMI$_3$ is shown direct band gap nature while other two compounds shown indirect band gap because of mismatching in CB minima and VB maxima at same crystal momentum. For the detail of band structure density of states (TDOS) and partial density of states (PDOS) are calculated, which shows different elements contribution in the form of orbital and states to VB as well as CB.

Optical properties are also calculated for AMX$_3$ using GGA scheme. These properties are reflectivity optical conductivity, dielectric constant, absorption, co-efficient and refraction. All the compounds showed good absorption co-efficient $\alpha$ ($\omega$), the graphic line of absorption co-efficient $\alpha$ ($\omega$) for AMI$_3$ is very effective for absorbing many wavelengths and can be used as an absorbing material.

The overall the suitable compound in our research study is methyl-ammonium iodide (AMI$_3$) which has extraordinary electronic and optical properties especially for inexpensive solar cell technology.

According to background and present study of methyl-ammonium lead halide of (MLH), this material has outstanding properties and the more and more study is important for commercialization MLH in future optoelectronic applications.

5. References

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