

The Ab Initio Study of Electronic and Optical Properties of $\text{CH}_3\text{NH}_3\text{ZnI}_3$ Perovskite Solar-Cell Material

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Abstract - Zinc oxide (ZnO) is a direct wide-bandgap semiconductor with high exciton binding energy of ~60meV. In search for lead free perovskite material, considering the application of ZnO in solar cell, we studied the electrical and optical property of a new Zn based perovskite materials namely methyl ammonium zinc triiodide ($\text{CH}_3\text{NH}_3\text{ZnI}_3$). We also compared the results with more popular methyl ammonium lead triiodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) used in perovskite solar cells. The band gap and x-ray diffraction data were also analyzed and compared. It was observed that the $\text{CH}_3\text{NH}_3\text{ZnI}_3$ absorbs electromagnetic radiation in far UV region. From the X-ray diffraction pattern, it was clear that $\text{CH}_3\text{NH}_3\text{ZnI}_3$ retains the original cuboctahedral crystal structures as $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Key Words: Semiconductor, perovskite, $\text{CH}_3\text{NH}_3\text{ZnI}_3$, simulation, DFT

1. INTRODUCTION

The development of halide perovskite solar cells is as rapid as the technology is proving successful [1]. The hybrid halide perovskites are a class of semiconductors of the empirical formula ABX_3 with high absorption coefficients and large carrier mobilities[2]. Research on these compounds dates to the 1920s. The most widely used hybrid perovskite solar cell material is methyl ammonium lead iodide $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI). A breakthrough in durability was the fabrication of $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based all solid- state solar cells, which demonstrated superior stability and an improved efficiency of 9.7%. Despite significant development of highly efficient hybrid solar cells, a rising concern is the toxicity of lead based perovskite solar cells, which has potential to inflict harm upon both the human body and the natural environment. To fabricate environmentally benign solar cells, it is essential to develop toxic lead free perovskite materials and maintains reasonable power conversion efficiencies as the previously mentioned Pb-based light-harvesting materials. In our work we investigated the electrical and optical properties of Zn based perovskite material. We choose $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite as a starting material and replace Pb with Zn. The band gap is not similar as the mostly used perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. There is a large difference in the bandgap although the XRD pattern showed similar peaks as the $\text{CH}_3\text{NH}_3\text{PbI}_3$.

2. COMPUTATIONAL METHODS

To study the structural, electronic and optical properties of $\text{CH}_3\text{NH}_3\text{ZnI}_3$, Zn atom was substituted for Pb in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ and the density functional theory (DFT) calculations were carried out using the Cambridge sequential total energy package (CASTEP) code[3]. Previous study shows the plane-wave pseudopotential calculations employing generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE), this parameterization was used for all the calculations in this research work, and Perdew-Wang 91 (PW91) exchange correlation functional appropriately describes the structures and the stabilities of the organometallic halide perovskites as evident by the experimental results[4]. As the organic cation and the inorganic anion electrostatically interacts with each other in the organic-inorganic ionic perovskite materials, this key contribution in the interaction was embodied by the ultrasoft pseudopotentials as represented by the typical DFT-GGA scheme[5] [6]. The plane-wave cutoff energies were fixed at 340 eV and a k-point lattice of $3 \times 3 \times 4$ of the Monkhorst- Pack grid was used for the Brillouin zone integration with 0.5 eV Gaussian smearing for all the calculations of $\text{CH}_3\text{NH}_3\text{ZnI}_3$ perovskite. We have carefully relaxed $\text{CH}_3\text{NH}_3\text{ZnI}_3$ structures by adjusting the lattice parameters so that the optimized structures gained no extra symmetries during the optimization calculations and converges with the total energy. Figure 1 shows the energy vs. optimization curve for single point energy calculations.

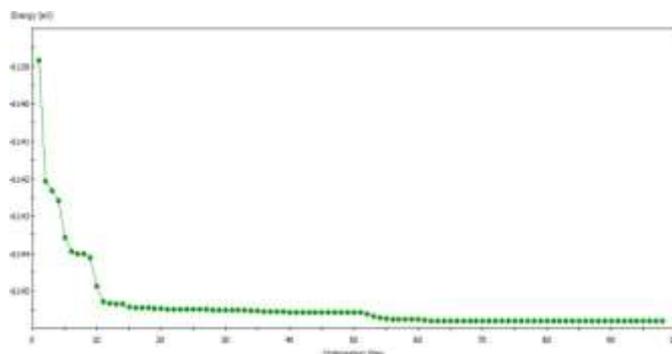


Fig-1: Energy vs optimization curve.

3. RESULTS AND DISCUSSIONS

Figure 2 illustrates the geometrically optimized $\text{CH}_3\text{NH}_3\text{ZnI}_3$ perovskite structure which is a tetragonal lattice and belongs to the $4/mmm$ space group. The Zn^{2+} cation forms six metal bond with its neighboring I- anions

and this ZnI6 are connected such as to give the cuboctahedra framework.

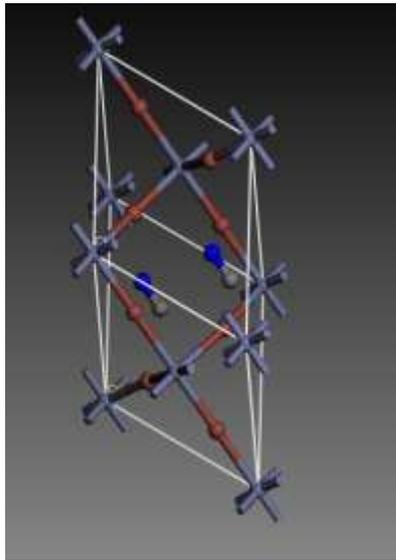
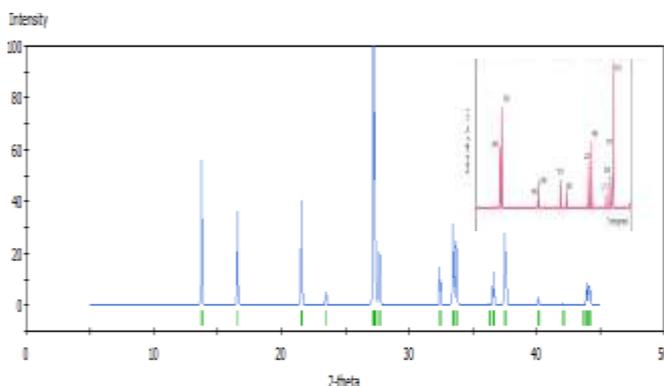


Fig-2: Structure of CH₃NH₃ZnI₃.

We have calculated the XRD pattern of our material and found that the highest peak for CH₃NH₃ZnI₃ was at 27.20 degree which compare to its similar counterparts perovskite structure CH₃NH₃PbI₃ was found to be at near 32.13 degree, experimentally [7]. In our whole investigation we didn't use any supercell structures instead we used the primitive unit



cell of the perovskite structure.

Fig-3: Calculated XRD pattern of CH₃ NH₃ ZnI₃ with the experimentally obtained XRD pattern of CH₃NH₃PbI₃ [7] in the inset.

There are some common planes in both CH₃NH₃ZnI₃ and CH₃NH₃PbI₃ structure, and that is due to CH₃NH₃I₃. The high intensity peak are attributed to the metallic PbI₂ or ZnI₂. From the X-ray diffraction analysis it is observed that CH₃NH₃ZnI₃ structures has {2 1 0}, {2 2 0}, {1 1 1}, {2 1 1}, {2 1 3}, {2 0 0}, {2 2 2}, {1 0 0} and {3 1 3} planes as shown in figure 3.

The calculations of the electronic band structure helps us to understand the character of prevailing bands near the Fermi level which in turns determines the properties of the material. This description of electronic band structure also

helps us to realize and predict certain characteristic features of the condensed matter systems. Figure 4 shows the electronic band structures of CH₃NH₃ZnI₃ and we can see that not a single one of the valance bands has crossed the Fermi level, although it has a metal atom in its structure. From the band structure it is observed that the shape of the conduction bands near to the Fermi level is parabolic which similar to the other semiconducting materials. The CH₃NH₃ZnI₃ has a direct bandgap of 0.340 eV whereas CH₃NH₃PbI₃ has a bandgap of 1.53 eV [7].

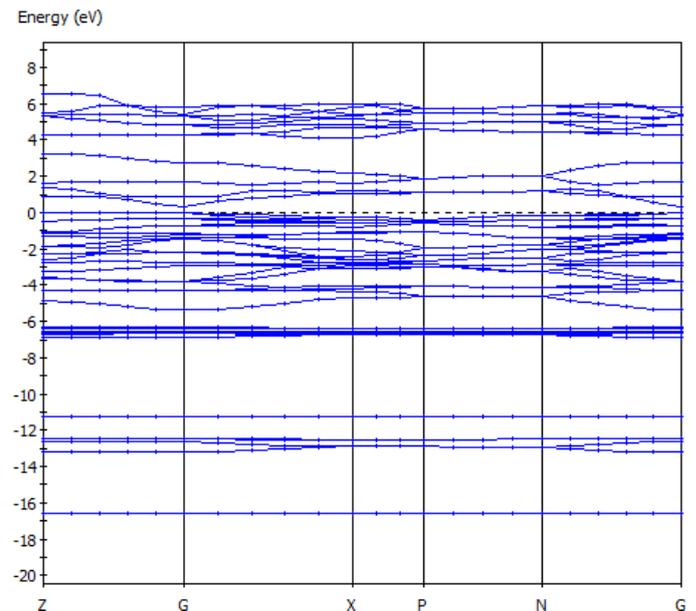


Fig-4: Electronic band structure of CH₃NH₃ZnI₃.

The distribution of available allowed energy states at any given energy interval of a quantum systems is represented by the density of states (DOS). Figure 5 shows the total and partial density of states of CH₃NH₃ZnI₃.

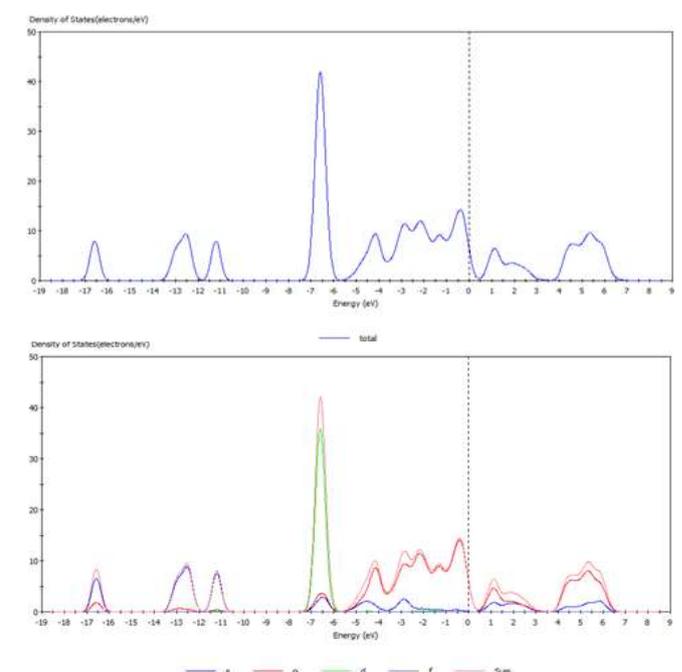


Fig-5: Total density of states (upper) and the partial density of state (PDOS) (bottom).

A DOS of zero means that no states can be occupied at that energy level. It can be seen from the partial DOS that the major contributions around the Fermi energy are mainly from the Zn 3d states and also the total DOS suggest that the Zn 3d states dominates the conductivity of CH₃NH₃ZnI₃.

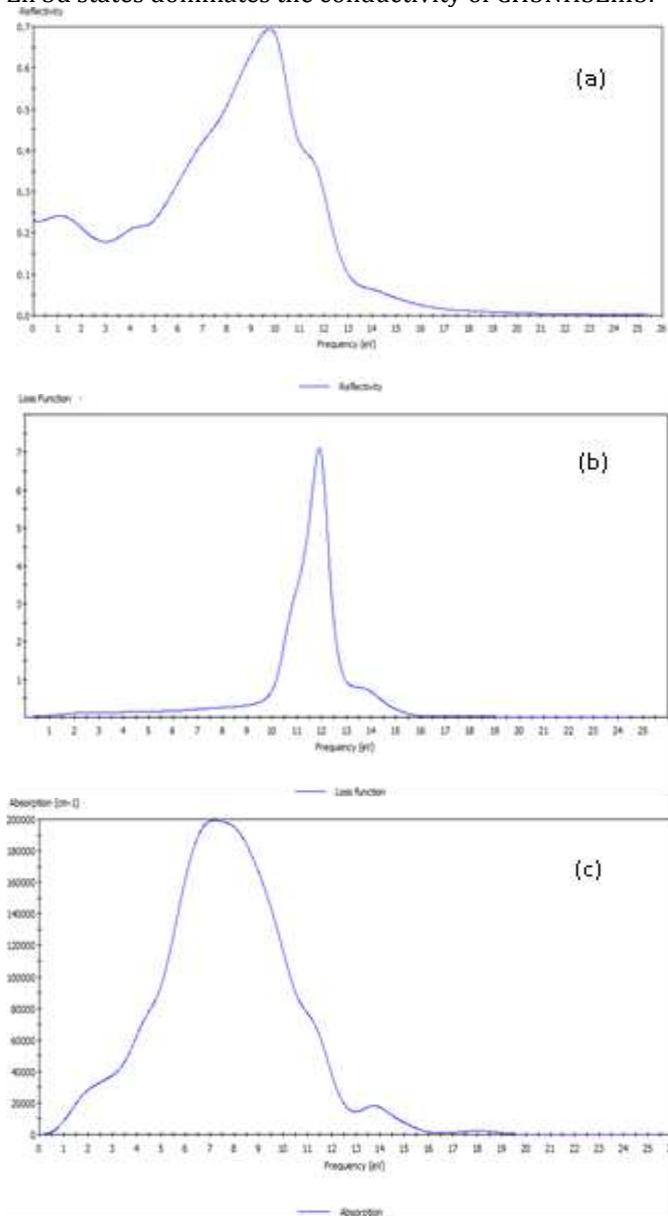


Fig-6: (a) The reflectivity curve, (b) loss factor and (c) UV-Vis-IR absorption spectra of CH₃NH₃ZnI₃.

Optical properties are important in solid state physics because the study of different optical characteristics of solids provides a correlation with the electronic band structure and helps us better understand the materials.

Figure 6 shows different optical parameters of CH₃NH₃ZnI₃ under electromagnetic radiation calculated for up to 25eV. The reflectivity spectrum shows that the material has maximum peak at 10 eV. This indicates that it has a low band gap. And it can reflect wave which lies at far-UV region which lies in between near to x- rays and farthest region from the visible light. The absorption curve shows that it has maximum peak at 7 eV. This compound has absorption

bands in the low energy range due to its metallic nature. The peak lies in the far UV region. In the energy-loss spectrums, the first peaks are found at 11.5 eV. It indicates that the material has a low band gap. So within the range of 122–200 nm the extinction of the absorbed light energy occurs.

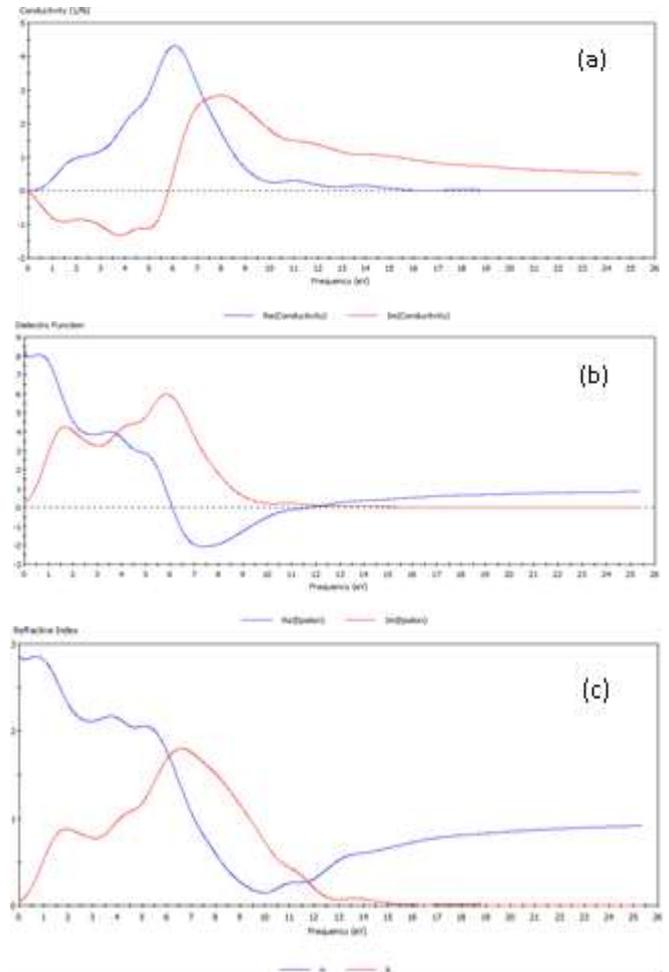


Fig-7: (a) The conductivity curve, (b) dielectric constant and (c) refractive index curve of CH₃NH₃ZnI₃.

From the conductivity curve it is seen that it has the maximum peak at 6 eV. After 6eV the conductivity falls and almost diminishes after 10 eV. The CH₃NH₃ZnI₃ perovskite material will not interact that much with the incident electromagnetic radiation which has energy more than 10 eV. From the dielectric function curve it is seen that the real and imaginary values are same at 4 eV and 12.25eV. The refractive index shows us the amount of dispersion of incident electromagnetic wave while it is passing through the material. So our material will disperse the wave which lies in the far UV region (6.2–12.4 eV) and the dispersion will be least at 10 eV. Further it will attenuate the incident waves which has frequency more than 10 eV (extreme ultra violet) as provided by the imaginary refractive index curve. After 25 eV no wave will be able to pass through the materials.

4. CONCLUSION

The structure-property relationship of CH₃NH₃ZnI₃ perovskite materials has been investigated in this research

work and it is found that the $\text{CH}_3\text{NH}_3\text{ZnI}_3$ was of tetragonal crystal structures with $4/mmm$ space group. The electronic band structure and the optical properties of $\text{CH}_3\text{NH}_3\text{ZnI}_3$ shows that $\text{CH}_3\text{NH}_3\text{ZnI}_3$ has a low band gap of 0.340 eV which is small compared with $\text{CH}_3\text{NH}_3\text{PbI}_3$. Also from the optical parameters it is seen that our investigated material shows the maximum absorption peak at far UV region. This indicates the proposed materials could be a potential photovoltaic light harvesting materials and is a good candidate in converting the sun radiation to electrical or heat energy. To improve our observed results the simulation work can be investigated for other exchange correlation functional considering GW many-body correction.

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