Comparative Study of the Structural and Electronic Properties of Orthorhombic CH₃NH₃PbI₃ Hybrid Perovskite for Solar Cell Applications

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Abstract

The structural and electronic properties of orthorhombic methyl ammonium lead iodide (CH₃NH₃PbI₃) were investigated using the first principles density functional theory within the local density approximation (LDA) and the generalized gradient approximation (GGA).The lattice parameters obtained using the GGA were slightly greater than that obtained using the LDA. The total density of states and the electronic structure of the compound show that it is a direct band gap semiconductor. Our results are in agreement with the previous experimental and theoretical results and suggests that orthorhombic CH₃NH₃PbI₃ compound is very promising in photovoltaic energy harvesting.

Keywords: Perovskite, density functional theory, band gap, solar cell, orthorhombic

1.0   INTRODUCTION

A perovskite is any material with crystal structure similar to the mineral called perovskite, which consists of calcium titanium oxide. The minerals were first discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and named after Russian Mineralogist L.A. Perovski (1792-1856). The general chemical formula for perovskite compounds is *ABX₃*, where A and B are two cations, often of very different sizes, and X is an anion that bonds to both cations. The A atoms are generally larger than B atoms [1,2].

Physical properties of interest to material science among perovskites includes superconductivity, magnetoresistance, ionic conductivity, and a multitude of dielectric properties, which are of great importance in microelectronics and telecommunication. Perovskites have been proposed for photovoltaic application with high conversion efficiency of up to 25.5%. They also have applications in laser light generation and light emitting diodes [2].

There have been various studies on CH₃NH₃PbI₃ perovskite in both tetragonal, orthorhombic and cubic phases [1, 3-10] both experimentally and theoretically. At temperature below 160 K, the orthorhombic phase is the stable phase [5,8]. Between the temperature of 165 K and 327 K, the tetragonal phase is stabilized [8]. Above the temperature of 327 K, the cubic phase becomes the dominant phase [8] at ambient pressure. The band gap of these perovskite CH₃NH₃PbI₃ compounds make them very promising for opto-electronic applications.

In this research work, the structural and electronic properties of the perovskite CH₃NH₃PbI₃ compound are investigated using the density functional theory implementing both the local density approximation (LDA) and generalized gradient approximation (GGA) with the van der Waals forces included. At the end we compare the results obtained using the two approaches. This will help to account for the relative accuracy of the van der Waals forces corrected LDA and GGA approximations in describing structural and electronic properties of this phase of the perovskites CH₃NH₃PbI₃ compound.

2.0   COMPUTATIONAL DETAILS

We employed Kohn-Sham equation within the framework of density functional theory to study the orthorhombic structure of CH₃NH₃PbI₃ (MAPbI₃) consisting of 48 atoms (4 C atoms; 24 H atoms; 4 N atoms; 4 Pb atoms; and 12 I atoms). Ab-initio density functional theory non-spin polarized calculations [11, 12] were performed in the local density approximation [13] and generalized gradient approximation of Perdew, Burke and Ernzerhof [14]. For these calculations, plane-wave self-consistent field method, as implemented in the Quantum-Espresso program package [15] were used. Plane wave basis sets were used to represent wave functions and the optimized density of valence electrons with kinetic energy and augmented density cutoff of 80 Ry and 320 Ry respectively (see Figure 1). At this cutoff, the total energy is converged to within 1 mRy/atom. Ion and valence electron interactions have been represented with scalar relativistic norm-conserving pseudo-potentials (PP) [16] obtained from Pseudo Dojo pseudopotential site [17]

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(with C-2*s, 2p;* N-2*s, 2p;* H- *1s;* Pb5*d, 6s, 6p;* I-5*s, 5p;* Ba-5*s, 6p, 6s;* Mg-2*s, 3p, 3s;Cl 3s, 3p* as the valence orbitals. We have implemented the Rutgers–Chalmers van der Waals density functional (vdW-DF) [18, 19] to take care of long-range dispersion forces between the CH_3NH_3 cation and the Pb-I anion structure. The van der Waals dispersion correction adds a semi-empirical dispersion potential to the conventional Kohn-Sham DFT potential. Brillouin zone integration was done over optimized 6 x 6 x 4 k-point grid (see Figure 2) sampled by Monkhorst-Pack scheme [20]. The optimization criteria for the ionic geometry relaxation were 0.0001 Ry for total energy and 0.001Ry/au for the Hellmann-Feynman forces.
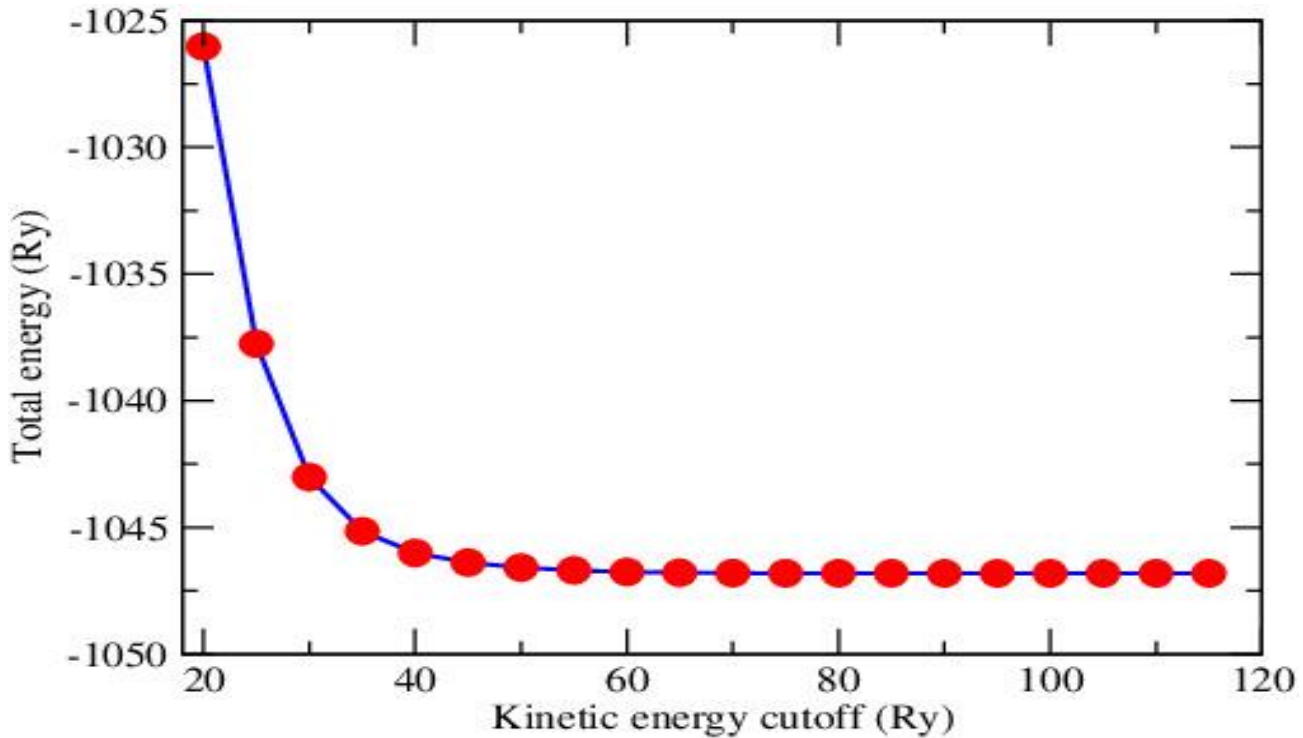

Figure 1: Graph of Total energy against kinetic energy cutoff
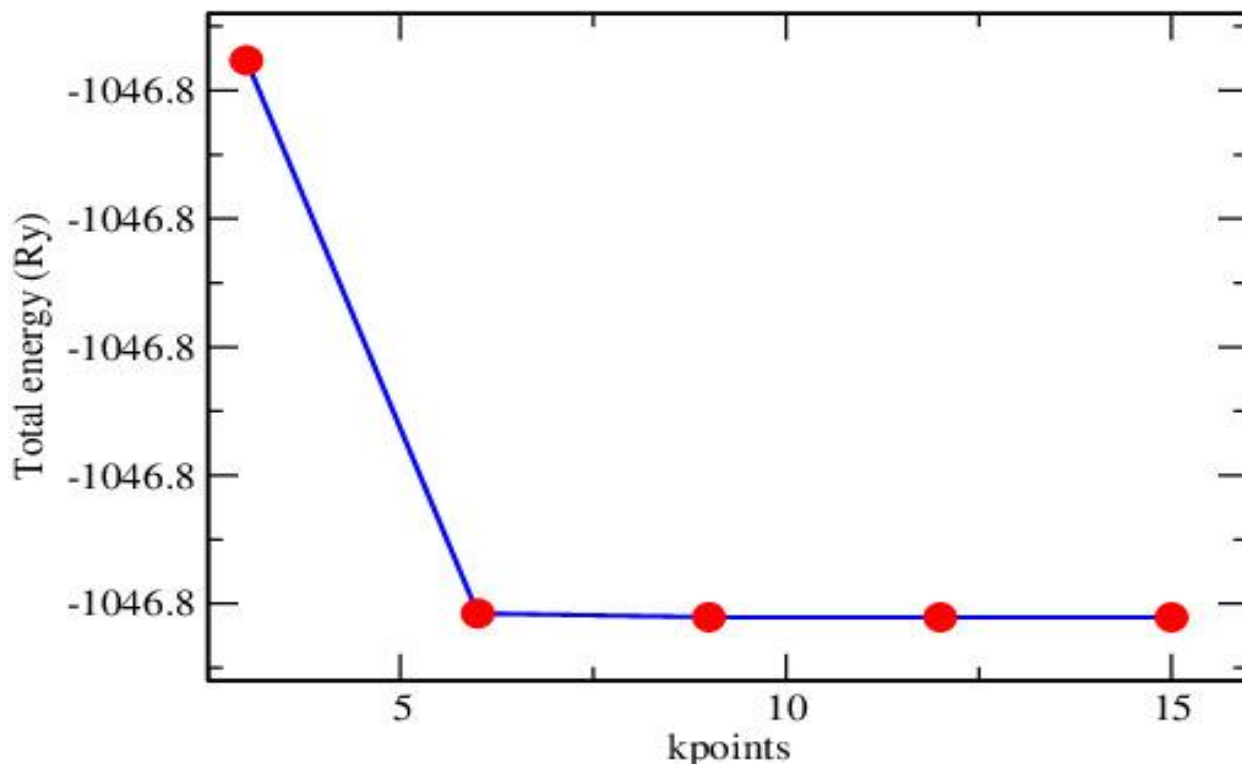

Figure 2: Graph of Total energy against K-points

3.0   RESULTS AND DISCUSSIONS
3.1   Structural properties
The crystal structure of the orthorhombic phase of $CH_3NH_3PbI_3$ perovskite is presented in Figure 3 while the lattice parameters obtained from our calculations are presented in Table 1. The structural parameters were obtained by the orthorhombic unit cell relaxation.

The N-H and C-H sub-systems are attached to the Pb-I sub-system mainly by the Van der Waals interaction captured in our calculation by introducing the Rutgers-

Chalmers van der Waals density functional theory approximations. Our lattice parameters compare well with the previous experimental and theoretical results. The lattice parameters obtained using the local density approximation (LDA) are slightly smaller than that from the generalized gradient approximations (GGA). This is perhaps due to the fact that GGA underestimates the electron interaction and by implication, the binding energy of the crystal.
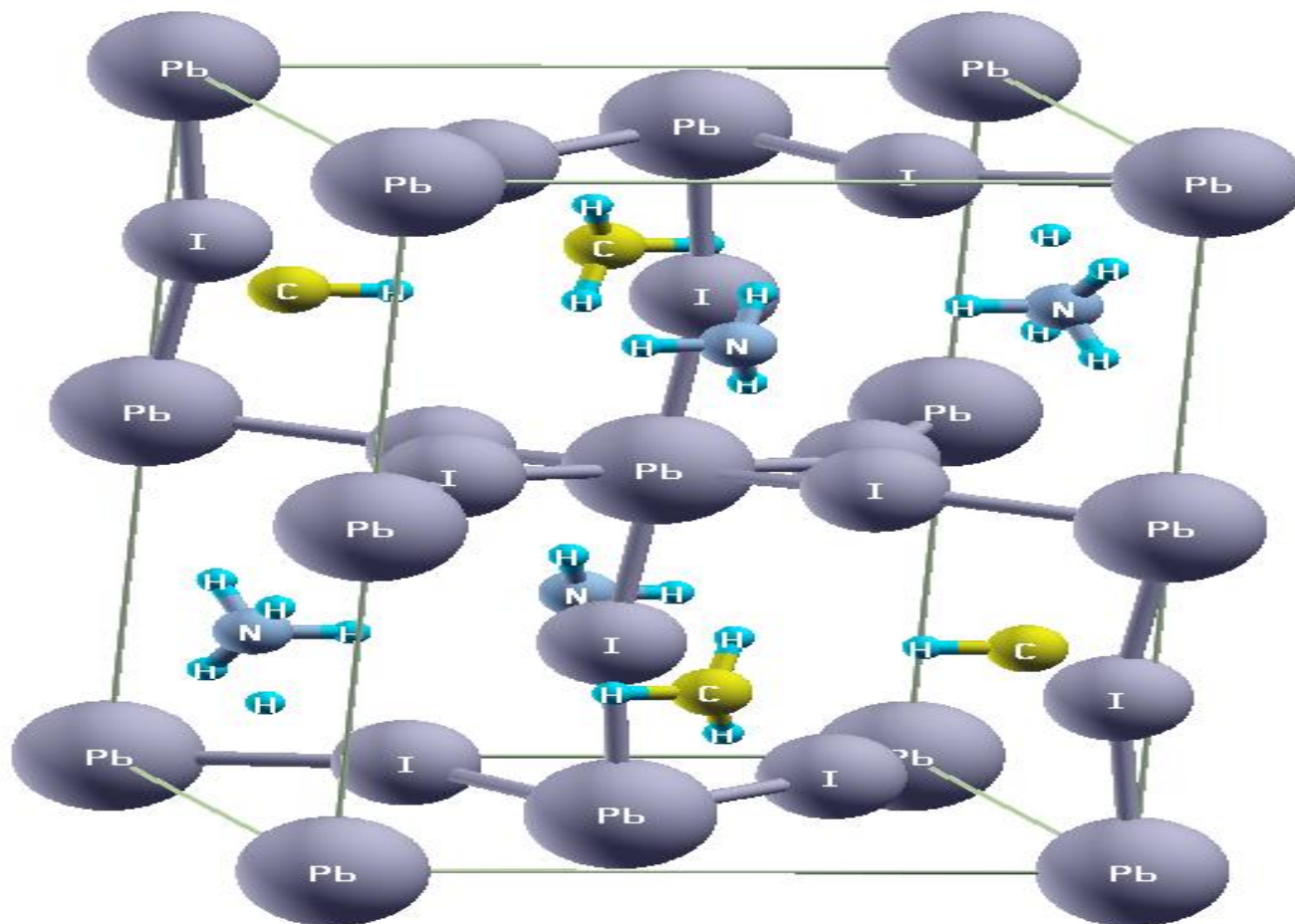

Figure 3: Orthorhombic crystal structure of methyl ammonium lead iodide

Table 1: Lattice parameters and band gap of orthorhombic methyl ammonium lead iodide

| Reference	a (Å)	b (Å)	c (Å)	Band gap (eV)
This Work (LDA)	8.60	9.30	13.03	1.9692
This work (GGA)	8.63	9.33	13.08	1.8896
Ref. [6] (Expt.)	8.84	8.56	12.58	-
Ref. [5] (PBE)	9.07	8.77	12.80	1.90
Ref. [4] (PBEsol)	9.04	8.35	12.66	-
Ref. [9] LDA	8.678	8.318	12.387	1.51

3.2   Electronic properties
In a pure semiconductor there are enough electrons to occupy the valence band fully while the conduction band is left completely empty. This yields an insulator rather than a conductor. Band structures can reveal some electrical properties of a material. The band structure of orthorhombic methyl ammonium lead iodide

were obtained at the equilibrium lattice parameters both for the LDA and GGA. Presented in Figure 4 and Figure 5 are the band structures of the orthorhombic structure of methyl ammonium lead iodide using LDA and GGA respectively. The size of the band gap obtained are recorded in Table 1. The electronic structure obtained for the orthorhombic methyl ammonium lead iodide crystal

using LDA and GGA show that the compound is a direct band gap semiconductor with a direct band gap of 1.9692 eV and 1.8896 eV respectively. The top of the valence band and the bottom of the conduction band occur at the Brillouin zone center (Γ-point).

The size of the electronic band gaps obtained in the orthorhombic methyl ammonium lead iodide using the LDA and GGA are further confirmed using the total electronic density of states presented in Figure 6 and Figure 7 respectively.
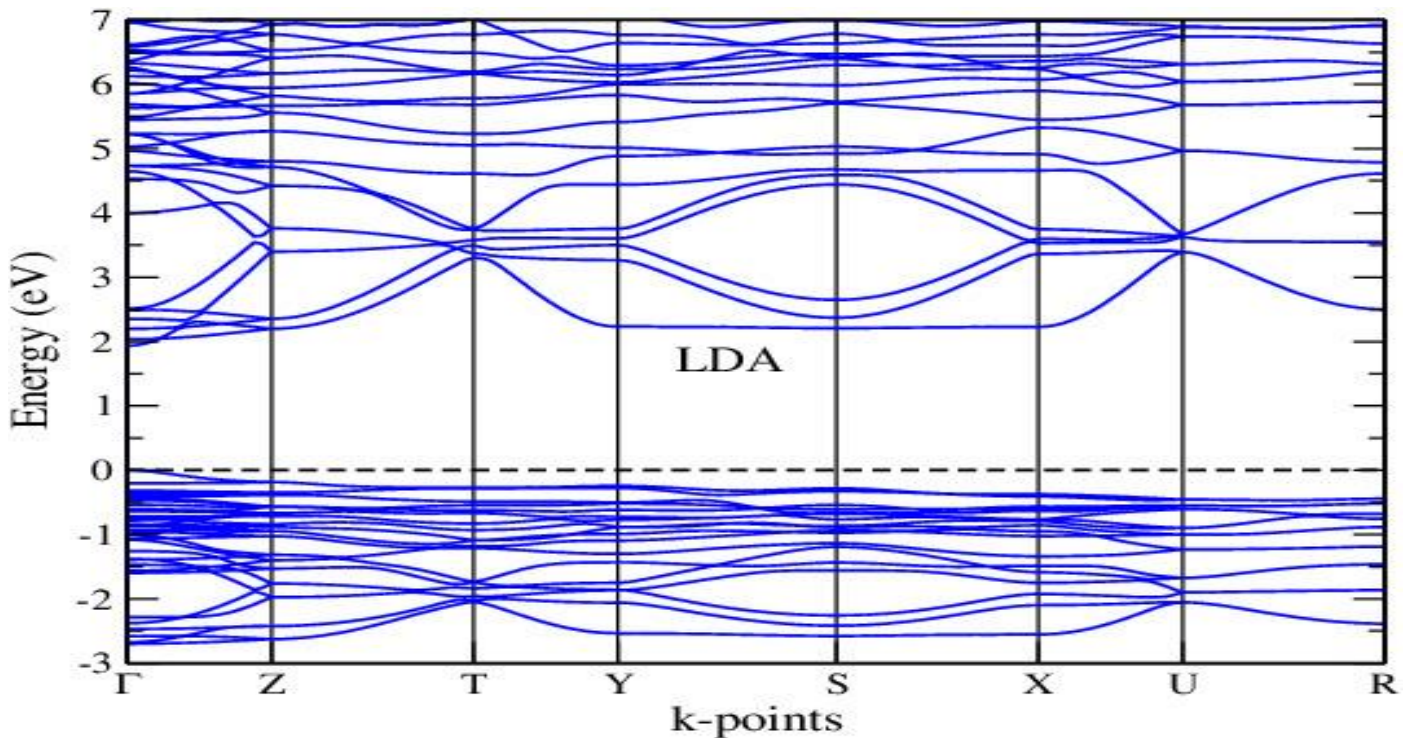
Figure 4: Electronic band structure of Methyl ammonium lead iodide using local density approximations (LDA).
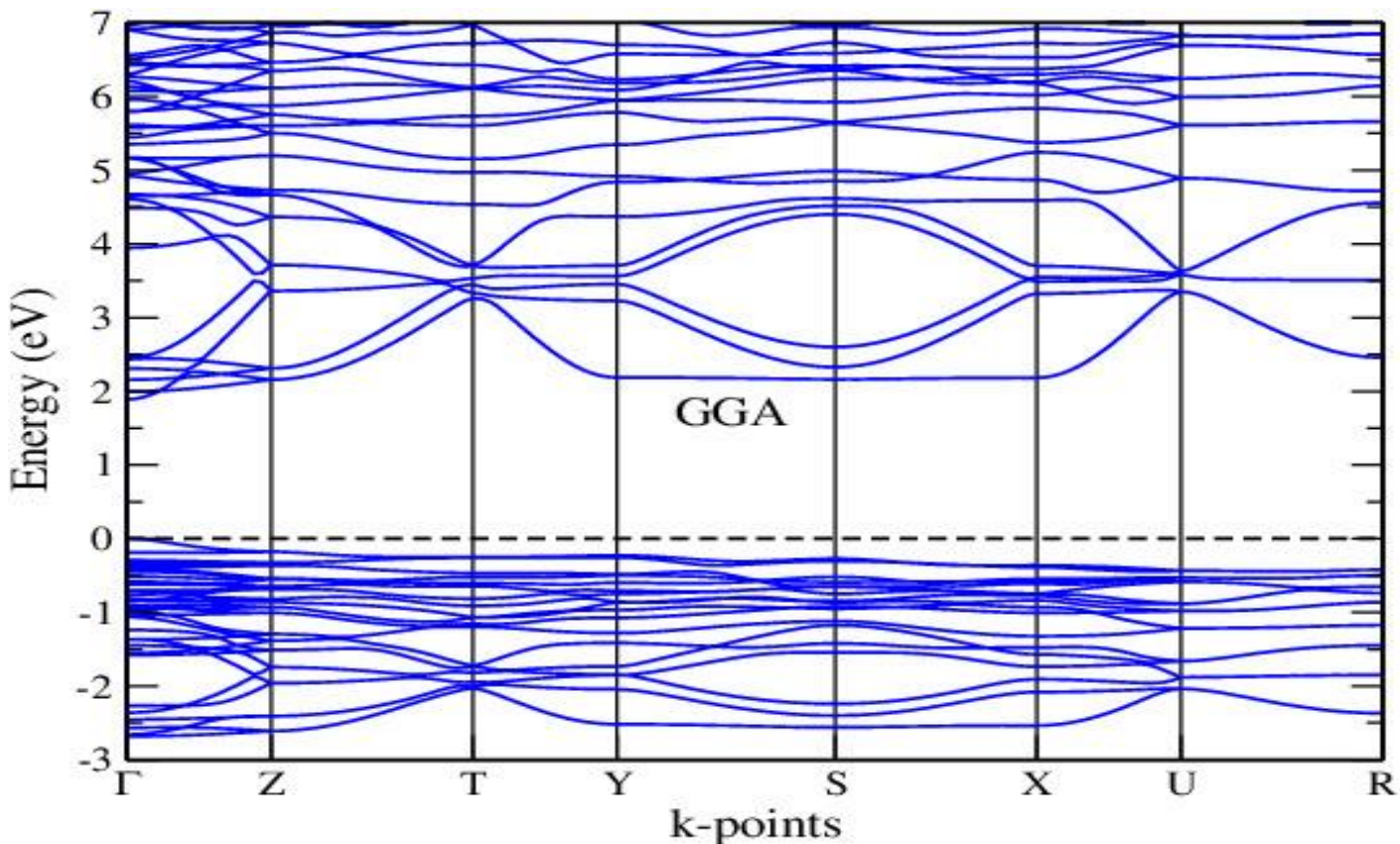
Figure 5: Electronic band structure of Methyl ammonium lead iodide using generalized gradient approximation (GGA).
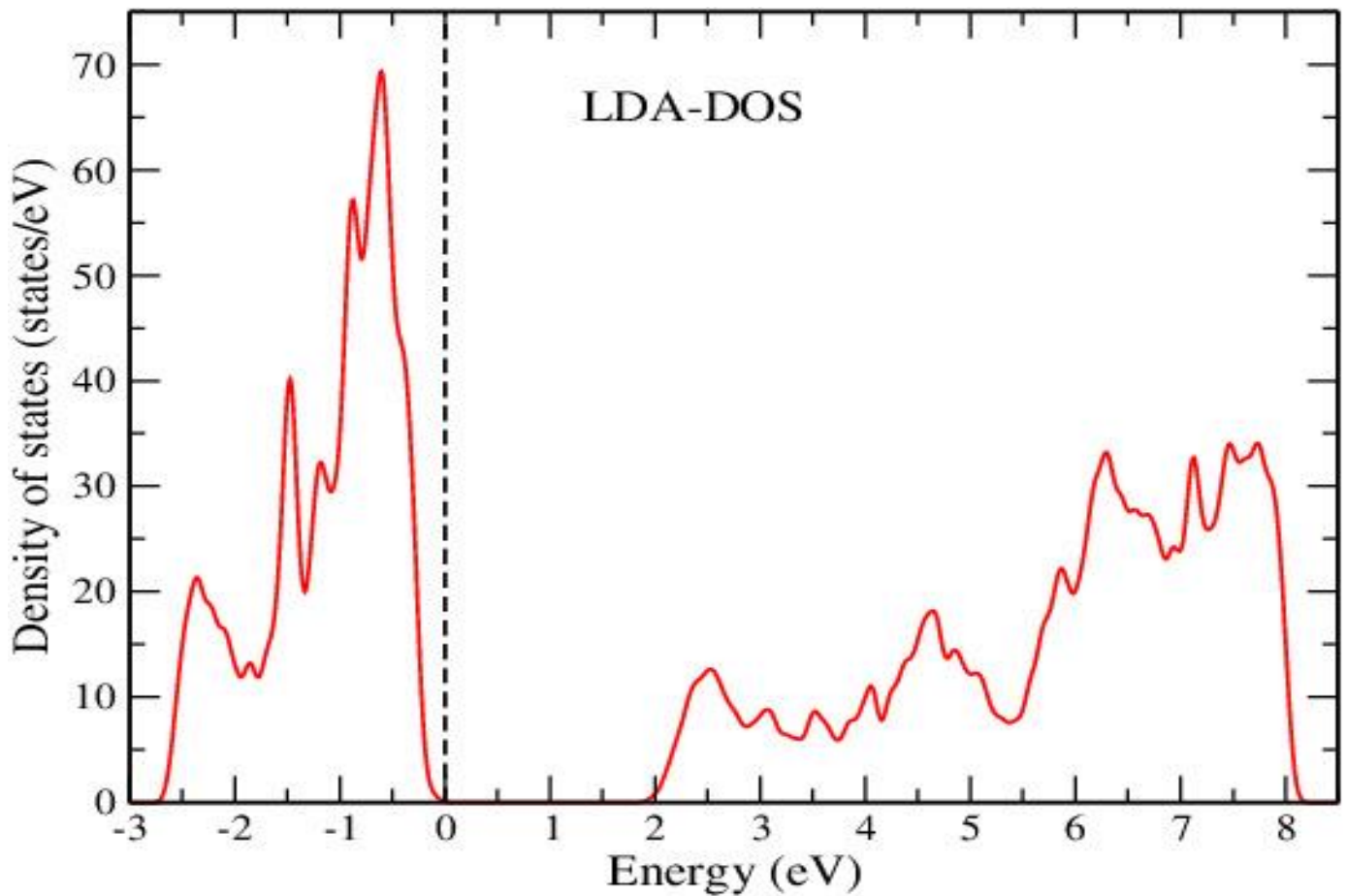
Figure 6: Density of States of orthorhombic phase of methyl ammonium lead iodide using Local density approximation (LDA).
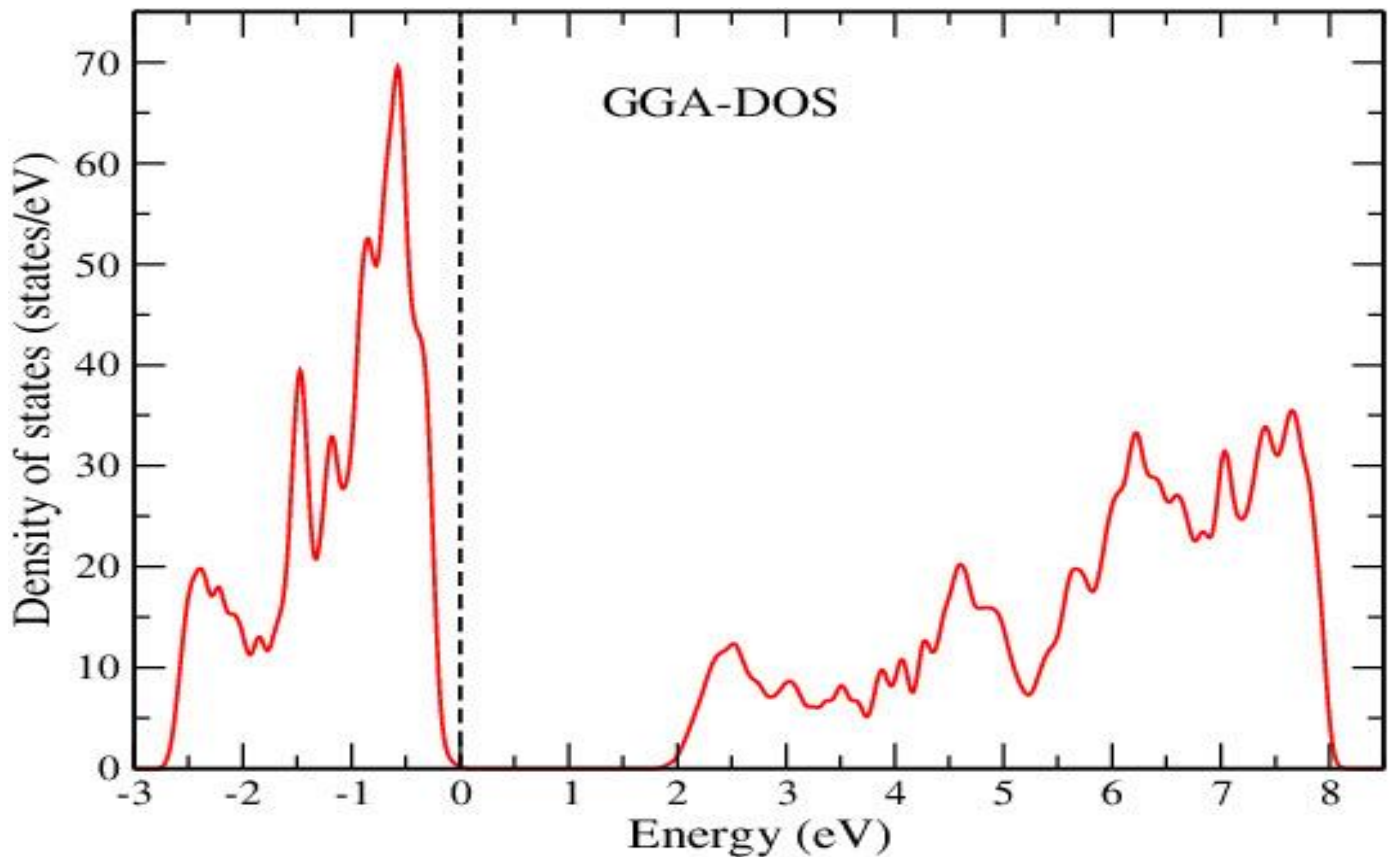

Figure 7: The density of states of orthorhombic phase of methyl ammonium lead iodide using generalized gradient approximation (GGA).

4.0   CONCLUSIONS

The structural and electronic properties of methyl ammonium lead iodide were investigated using the first principles density functional theory within the local density approximation and the generalized gradient approximation. The lattice parameters of the orthorhombic structure of the methyl ammonium lead iodide were computed using the local density approximation and the generalized gradient approximation. The total density of states and the electronic and structure of the orthorhombic methyl ammonium iodide was also calculated. Our results are in agreement with the available experimental and theoretical results and confirms that compound is very promising in photovoltaic energy harvesting.

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