THE ELECTRONIC BAND STRUCTURE AND DENSITY OF STATES ANALYSIS OF ELECTRON TRANSPORT MATERIALS FOR PEROVSKITE SOLAR CELLS.

Joy Sarkar, Rajat Biswas, Suman Chatterjee

Department of Physics, University of North Bengal, Raja Rammohunpur, Darjeeling, Siliguri-734013, India

Email: joysarkar2019@nbu.ac.in

Abstract

For investigating the atomic-scale calculation of perovskite solar cells (PSCs), a detailed model of interaction between the electrons and the junctions is very essential. Such atomic-scale level analysis is based on the quantum mechanical model. Therefore we need a Schrödinger equation which involves all the electrons with the associated junction potential. Here we consider the Schrödinger equation and solving it by full-potential linearized augmented plane wave (LAPW) method in Wien2k code through the Density Functional Theory (DFT). We have used generalized gradient approximation (GGA) given by Perdew-Burke-Ernzerhof (PBE) for the electronic band structure and Density of States (DOS) calculation of TiO_2 and ZnO which are used in perovskite solar cell as the electron transport layer. We obtained the value of the energy bandgap as ~2.934 eV for TiO_2 and ~3.119 eV For ZnO. We also determined the value of Fermi energy for both of the material. Finally, we compare the transport properties of TiO_2 and ZnO by analyzing their band structure and DOS diagrams.

Keywords: Perovskite solar cells, Density Functional Theory, Linearized augmented plane wave, Generalized Gradient Approximation, Density of States.

1. Introduction

Photovoltaic is a solar power technology that uses solar cells or solar photovoltaic arrays to convert light directly into electricity with the least amount of industrials waste and with no emission of harmful gases [1]. A large development in Photovoltaic energy utilization and generation has taken place in the first few years of the 21st century [2, 3]. Particularly in Japan and Germany due to a variety of reasons including the concerns of deteriorating earth atmosphere and global warming, this technology has seen a large increase in solar panel manufacturing and deployment world over [4]. In the last few years, about 30-40% growth in the sector is a great incentive for investment. Venture capitalists, entrepreneurs, and big industrial houses in the country are coming forward to establish industries in this area. In the Indian industrial world, technology is expected to make a big splash and solve the power crisis being faced in many states.

For developing a new-generation organic photovoltaic (PV) cells, Dye-sensitized solar cells (DSSCs) and organic bulk-heterojunctions (OBHs) appeared as an interesting component with unique easy property-tuning features. However, the power conversion efficiencies (PCEs) of both DSSCs and OBHs are largely behind from the silicon-based PVs due to their lower carrier mobility and limited optical absorption efficiency. As a result of this scientists searched for new-generation solar cells with higher efficiencies for the past few decades. For the development of new-generation solar cells, organo-metal halide perovskites have the power to arouse interest and become remarkably attractive photovoltaic materials. Miyasaka et al. reported the first perovskite solar cell (PSCs) with a PCE of 3.81% [5] in 2009. After two years Park et al. raised the PCE to 6.5% [6]. Next, Snaith et al. demonstrated high-efficiency perovskite solar cells with PCE reaching 10.9% till 2012 [7]. An amazing growth from 10.9% to 20.1% [8] in PCEs of perovskite solar cells have shown during the past successive years which provide a unique platform exploring new-generation photovoltaic systems.

Perovskite solar cells are also cheaper to produce than silicon solar cells and very efficient in absorbing light. Compared to Silicon, it uses less material to absorb the same amount of

light resulting in cheaper solar power. Besides, the fabrication process of PSC is quite simple and material costs are moderate, a lot of experimental research work has been carried out primarily for achieving better efficiency of PSC [6, 7]. This includes the study of variation of different components experimentally and finding out their effect on efficiency. However, a comprehensive analysis of device design based on its working principle is comparatively less abundant. Thus a theoretical study of the transport mechanism is necessary for achieving better efficiency by predicting the proper material design of PSCs. From complete knowledge of the transport procedure, we can predict proper electron conduction mechanism across the interface of PSCs and be able to form a high-performance perovskite solar cell. Though PSCs hold a lot of great promising quality which can give us a new path to the research of renewable energy for the better sake of mankind, it suffers from some disadvantages like it breaks down very quickly when exposed to heat, snow, moisture, etc. Some other problems like hysteresis of current-voltage characteristics and the device structure also require improvements.

The most successful approach is Density functional theory (DFT) invented by Kohn and coworkers more than 50 years ago [9] for investigating the electron transport phenomenon across the interface (e.g. between perovskite & electron transport layer and perovskite & hole transport layer) of PSCs. In this article, we have demonstrated the electronic and optical properties of some materials used as an electron transport layer (ETL) in perovskite solar cells using Density Functional Theory. All of the computational work done in this analysis has been implemented by using the WIEN2k software. The WIEN2k program is developed by Blaha, Schwarz [10] which implements the full-potential linearized augmented plane wave method which we have used for the calculations of band structure framed within Density functional theory (DFT). We have analysed these calculations from standard lattice parameters by using Generalized Gradient Approximation (GGA) given by Perdew-Burke Ernzerhof (PBE) [11]. After that by optimizing the lattice parameters, we have calculated the electronic properties which include band structure and density of states (DOS).

2. Computational Study

The selection of Perovskite and tandem Perovskite materials will be done based on electronic band structure analysis. For determining the correct component as ETM (Electron Transport Material) in PSCs, we calculated structural and electronic properties of TiO_2 (Rutile)and ZnO (Wurtzite) by using full-potential linearized augmented plane wave (LAPW) approach by implementing DFT in WIEN2k code [10]. The lattice parameters and the geometry of TiO_2 and ZnO used in this research are shown in table 1.

Table 1

The Geometry of ZnO and TiO_2

	ZnO	**TiO_2**
Lattice	Hexagonal a=b=3.2495 Å c=5.2069 Å α=β=90°, γ=120°	Body Centered Tetragonal a=b=4.51 Å c=2.93 Å α=β=γ=90°
Symmetry Information		
Space Group	186	136
Hermann-Mau-guin	P63mc	P42/mnm

The LAPW method is one of the most accurate methods for calculating electronic structure for the crystals. The method is based on DFT for the treatment of exchange and correlation and it uses the local spin density approximation (LSDA). There are various forms of this LSDA potential from which we have used generalized gradient approximation (GGA) given by Perdew-Burke-Ernzerhof (PBE) [11]. Like most of the energy band calculation methods, In the LAPW method, the basic assumption is of partitioning the unit cell into (I) non-over-lapping atomic spheres(Centered at the atomic sites) and (II) an interstitial region as shown in fig.1.

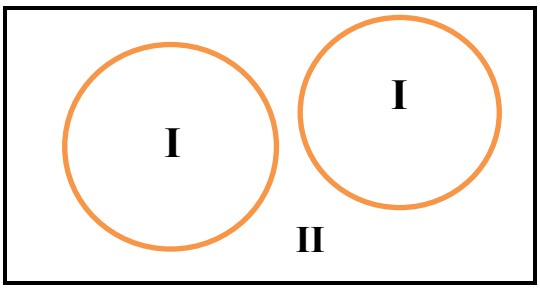

Fig.1: Partitioning of the unit cell into atomic spheres (I) and an interstitial region (II)

Inside atomic sphere (region I), of radius R, a linear combination of radial functions times spherical Harmonics $Y_{lm}(r)$ is used

$$\Phi_{k_n} = \sum_{lm}[A_{lm,k_n}u_l(r,E_l) + B_{lm,k_n}\dot{u}_l(r,E_l)]\,Y_{lm}(\hat{r}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

Here,$u_l(r,E_l)$ is the regular solution of the radial Schrödinger equation for energy E_l and the spherical part of the potential inside the sphere, $\dot{u}_l(r,E_l)$ is the energy derivative of u_l evaluated for the same energy E_l. A_{lm} and B_{lm} are the coefficients and functions of k_n.

In the interstitial region (region II) a plane wave expansion is used such that

$$\Phi_{k_n} = \frac{1}{\sqrt{\omega}} e^{i\boldsymbol{k_n}\cdot\boldsymbol{r}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(ii)}$$

Where $k_n = k + K_n$ and K_n are the reciprocal lattice vectors and k is the wave vector inside the first Brillouin zone. Each plane wave is improved by an atomic-like function in every atomic sphere.

The solutions to the Kohn-Sham equations used in wien2k code are expanded in this combined basis set of LAPW's as mentioned above in equation (i) & (ii) according to the linear variation method is given by

$$\Psi_k = \sum_n c_n \Phi_{k_n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(iii)}$$

Where c_n is a coefficient calculated by Rayleigh-Ritz variational principle. The mode of calculation of our work is fully relativistic core and scalar relativistic valence (RELA) which includes a new mode for coulomb integral consistent of 3/8 Simpson combinations. The number of symmetry operations performed is 16 for TiO_2 and 12 for ZnO. The wave functions expansion in the muffin-tin spheres (spherical region) has been carried out by choosing l_{max}=10, whereas the convergence of eigenvalues in the interstitial region is controlled by taking the cut-off parameter $R_{mt}K_{max}$=7.0. Where R_{mt} is the smallest atomic sphere radius in the unit cell and k_{max} is the magnitude of the largest K vector in equation (iii). In this work, we have used 1000 KGEN values from where 76 k-points (ZnO) and 70 k-points (TiO_2) generated in the irreducible Brillouin zone for the calculations of structural and electronic properties. The separation between valence and core states was achieved by using cut-off energy as -7.0 Ry. Finally, for running the program we invoke the self-consistency cycle (SCF)in which the calculations are acquired by following the steps such that LAPW0 (generates potential from density) then LAPW1 (calculates eigenvalues and eigenvectors of valence bands) after that LAPW2 (calculate valence band density from eigenvectors-RHO file) followed by LCORE (computes core states and densities) and at last MIXER which mixes the input and output densities.

3. Results and Discussion

3.1. Structural Properties

There are several polymorphs of TiO_2 such that Anatase, Rutile, Brookite, Akaogiite but amongst all Rutile is a mineral which composed of titanium dioxide (TiO_2) and known as the most common natural form of TiO_2. This form of TiO_2 obtained the highest value of the refractive index at visible wavelengths. It also exhibits a particularly high dispersion and a large birefringence. In the crystal structure of Rutile the coordination number of Ti cations is 6 i.e. they are surrounded by 6 oxygen atoms. On the other hand, the O anions have a coordination number of 3 forming trigonal planar coordination.

Whereas ZnO has a wurtzite type structure, which is non-centrosymmetric (i.e. lacks inversion symmetry).Due to this property, the wurtzite type crystals show piezoelectricity and

pyroelectricity. The semiconducting ZnO has several favourable properties for using as charge transport material in solar cells, including good transparency, high electron mobility, wide bandgap, large bond strength, and large exciton binding energy (60 meV)[12] at room temperature. From Fig.2 we found that the structure of ZnO is composed of two interpenetrating closely packed hexagonal (hcp) lattices consisting of one type of atom (Zn or O) moved concerning each other along threefold c-axis. The structure composed of tetrahedrally coordinated Zn^{2+} and O^{2-} and this type of coordination gives rise to the above mentioned non-centrosymmetric structure. In wurtzite type hexagonal ZnO; each anion is enclosed by four cations at the corners of a tetrahedron.

In Fig.2 the Violet spheres denote Zn atoms Red spheres represent oxygen atoms and Blue spheres corresponding to Ti atoms.

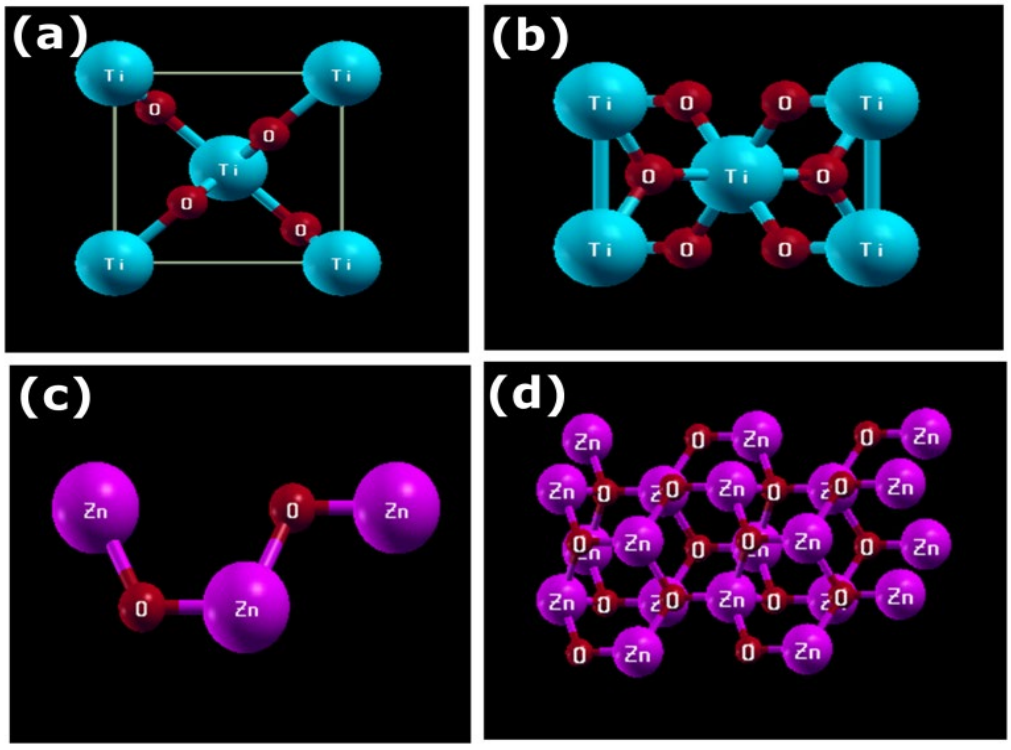

Fig.2. Crystal structures of (a) & (b) Rutile TiO_2 (c) & (d) wurtzite type ZnO with different orientations.

3.2. Electronic properties

The theoretical calculation of the materials is based on Electronic band structure and DOS analysis. The study of band structure helps us to find the range of electron energy of the corresponding atoms in association with the energy bands of the considered materials. [13,14]Electronic band structure and DOS of TiO_2 and ZnO have been calculated using exchange potential PBE-GGA linked with Density functional theory. The calculated band diagrams of Rutile TiO_2 and Wurtzite ZnO are shown in Fig.3. From the figure, it is obtained that the electronic band structure of both the materials has a direct bandgap with a conduction band maxima (CBM) and the valence band minima (VBM) at the same Brillouin zone point.

In Condensed matter physics we described the density of states (DOS) of a system as the number of states per unit interval of energy at each energy level available to be occupied. High DOS at a specific energy level indicates that there is a huge no of states available for the occupation of electrons whereas in the DOS graph a DOS of zero means that there are no states to occupy. For the case of atoms or molecules in a system (unlike isolated systems) we did not obtain a discrete density distribution but we get a continuous spectrum of the density of states as shown in Fig.3. So it is very important to study the density of states (DOS) of TiO_2 and ZnO for deeper study of electronic band structures. In this research, we performed a DOS study of these two types of electron transport materials and the results are as shown in Fig.3.

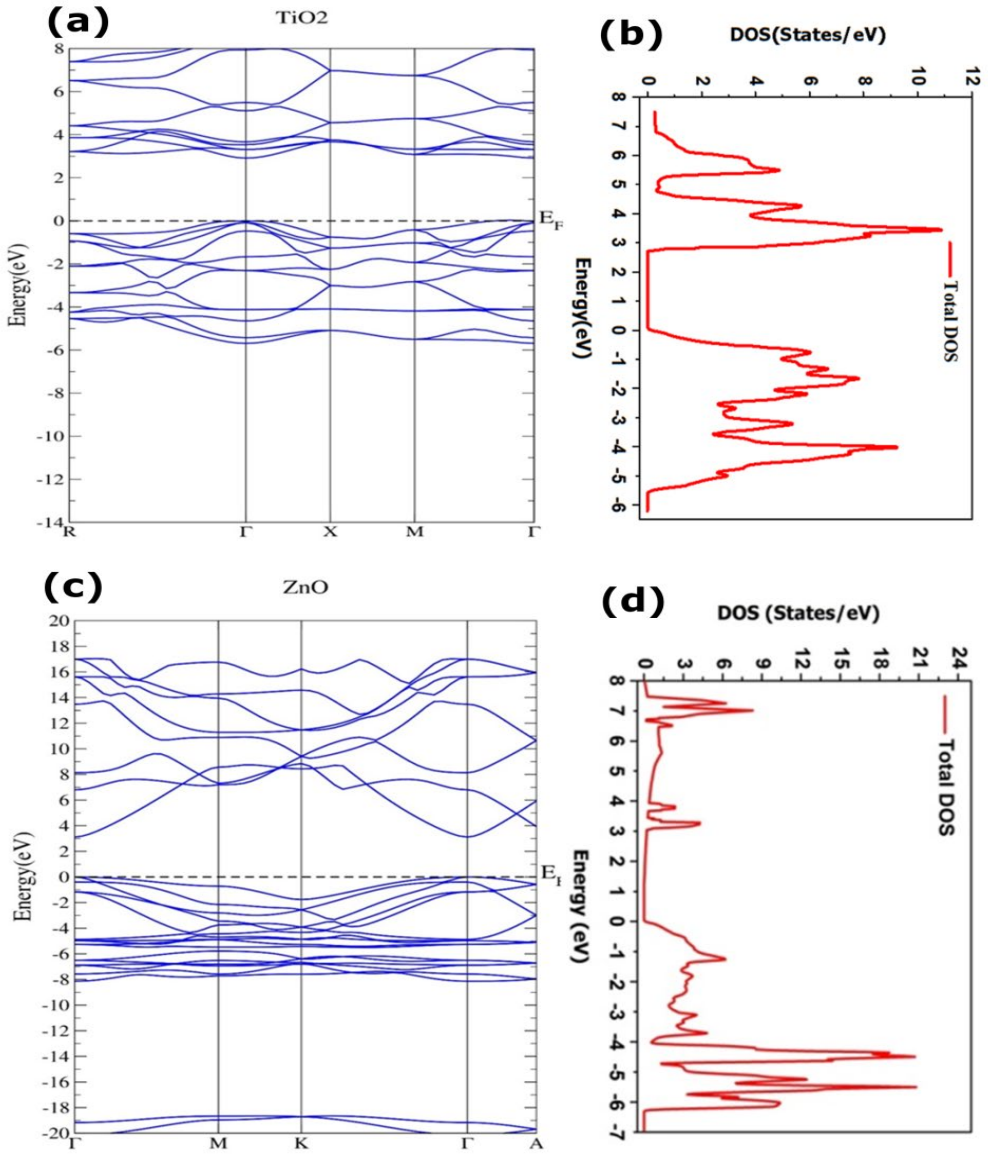

Fig.3. (a) The electronic band structures, (b)Density of States of Rutile TiO_2,(c)The electronic band structures, (d)Density of States of wurtzite type ZnO calculated with PBE-GGA.

The Bandgap was obtained as ~2.934 eV for TiO_2 and ~3.119 eV For ZnO. Calculated Fermi energy for TiO_2 is 0.422018 and 0.30961 for ZnO. The band program automatically scans over the high symmetry k-points which form the Brillouin Zone boundary. The list of allowed k-points for this study are, TiO_2 - BCC Gamma, M, R, X (K-points) ZnO-hexagonal Gamma, A, K, M (k-points). From the Fig 3, it is obtained that TiO_2 has a very high value

of DOS at both conduction and valence band region which indicates that a large number of states are available for electron transfer from LUMO layer of perovskite to the CBM of TiO_2 transport layer which corresponds to a great performance of the cell. But a high DOS at valence band also indicates that there may be a huge chance of electron recombination to the valence band from the conduction band of TiO_2 which is known as electron trapping of ETM. Now at low temperatures, the mobility of ZnO is higher than that of TiO_2 [15]. It is found that Electron carrier mobility of ZnO is 200-300 cm^2 $V.S^{-1}$ which is much higher than TiO_2 which has been noted to be 0.1-4 cm^2 $V.S^{-1}$[16-20]. Due to low electron nobilities and transport properties, the electron recombination rate is higher for TiO_2. In the other hand from Fig.3, it can be noted that due to very high electron mobility and moderately high density of states (DOS) at the conduction band region results to a comparatively lower probability of electron recombination for ZnO, which can be attributed to the higher performance of ZnO. Therefore it is expected that Wurtzite (ZnO) can be used as a good electron acceptor and transparent material alongside the novel TiO_2 in the study of perovskite solar cells.

4. Conclusion

The theoretical approach has been extensively used to design new solar cell materials. It should be noted that a promising solar cell absorber must simultaneously meet several criteria such as structurally stable, direct bandgap, suitable bandgap value, high optical absorption coefficient, small effective masses for electrons and holes, high electronic dimensionality, defect tolerance, etc. Only the full understanding of all these issues can predict whether an absorber and proper electron conduction through the ETL, HTL and the electrodes can produce high-performance solar cells. It is anticipated that the theoretical approach will continue to make contributions to the research of perovskite solar cell materials. The transport of electrons and holes through the different phases in a cell and the grain boundaries play an important role in higher efficiency. By analysing Band structure and density of states of TiO_2 and ZnO, we found that these two materials have shown a very similar nature to PSCs as

wide bandgap semiconductor electrodes. Although, TiO_2 is the most commonly studied oxides used as ETL in perovskite solar cells because of its fascinating optoelectric properties, from the theoretical analysis it can be predicted that ZnO also has some very interesting properties so that using ZnO individually or along with TiO_2 as ETL in PSCs might bring us satisfying outcomes.

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