Physics

ABSORPTION SPECTRA OF CU$_2$WS$_4$: A HYBRID FUNCTIONAL APPROACH

Narendra Kumar*
Piyush Dua**

ABSTRACT

It has been predicted that Tungsten (W) and Molybdenum (Mo) based materials increase the chemical activity for photo-electrochemical water splitting. Cu_2WS_4 is one of the semiconductors with a band gap of 2.0eV which is more than sufficient to absorb visible spectrum of sun light for hydrogen production. In Cu_2WS_4, it has been shown that W contributes mainly in absorption and S & Cu contribute in emission spectra based on a recently developed approach which involves only one arbitrary parameter. In our method, a tunable component of exact exchange has been introduced for the relevant Kohn–Sham orbitals for optimum results for lattice parameter and band-gap determination.

Keywords: Absorption spectra, d-electron systems photo-catalysts, photo-electrode.

INTRODUCTION

Hydrogen has been considered to be the fuel for future. Hydrogen can be produced through various resources including fossil fuels, such as coal and natural gas, nuclear and biomass and other renewable energy technologies, such as wind, solar, geothermal and hydroelectric power [1]. However, currently, the greatest technical challenge to hydrogen production is cost reduction. Therefore, it is urgent to discover and develop less expensive and environment friendly methods for hydrogen production and for which a few materials are required which can fulfill all the requirements of hydrogen generation process such as cost reduction with high life time. Solar hydrogen production from water without non-regenerated energy consumption and CO_2 emission has been believed to be of great economic and environmental interest, considering the issues of energy cost and environment protection. As one of the several ways for solar hydrogen production, semiconductor-based photocatalytic water splitting into H_2 and O_2 has attracted intense research interest [2, 3]. The importance accorded to extracting hydrogen

*Narendra Kumar is a Research Scholar in the Department of Physics, Mewar University, Chittorgarh, Rajasthan.

** Piyush Dua is a Faculty at the Department of Physics, University of Petroleum and Energy Studies, Dehradun, Uttarakhand.

from water is driven by the requirement to find a renewable, sustainable and environmentally safe alternative energy source. Hydrogen is considered as a viable option to today's fossil fuel-based energy source especially when it is produced from water and only sunlight is the energy input [4]. Hydrogen is an energy carrier, when used in fuel cell which combines it electrochemically with oxygen from air thus producing water and energy in the process [5]. This completes the consumption and regeneration cycle of hydrogen.

Photo-electrochemical (PEC) water splitting has the potential to be an efficient and cost effective way to produce hydrogen where the photo-electrode in PEC system absorb sunlight and split water directly into hydrogen and oxygen. The main work in PEC water splitting is still concerned with increasing the efficiency and stability of the photoactive materials [6, 7] to achieve the required efficiency target of 10% that will be viable for commercialization [8].

At the moment stable photo-electrode materials based on metal oxide have rather low efficiency of several percent [9, 10] while high efficiency materials based on multi-junction conventional semiconductor can achieve slightly above 10% [11,12], but get degraded within a short time.

Since the introduction of PEC water splitting process, the field has been developed as a separate research area to study different kinds of semi-conducting materials which have been developed as photo-catalysts for hydrogen production for water. Out of the materials identified for PEC water splitting, most of them could work in the ultraviolet region which can occupy a small fraction of the incoming solar energy. A lot of materials have been proposed that can work under visible light. A big list of materials is available which can provide an efficiency of about 7%, under visible which is still far from the starting point for practical application which is 30% at 600nm [13]. Therefore, it is still a challenge to identify such material which can fulfill all the requirements for PEC water-splitting process.

The aim of PEC material fabrication is to design a photo-electrode that has the potential to satisfy most of the requirements viz. (a) sufficient visible light absorption i.e. band gap in the range of 1.8-2.2 eV, (b) efficient separation and fast transport of photo-generated electron-hole pairs to prevent recombination, (c) favorable conduction and valence band edge position with respect to redox potential of water, (d) non-corrosive and high chemical stability in the electrolyte, and (e) low cost. Large band gap semiconducting oxides such as TiO_2, WO_3, $SrTiO_3$, $BaTiO_3$, SnO_2, ZnO etc. are stable in aqueous electrolyte but absorb in UV region which is only about 3% of the solar spectrum, whereas small band gap semiconductors such as Si, GaAs, InP, CdTe, CdSe, CuO etc. and optimum band gap semiconductor viz. Cu_2O have the potential to absorb visible part of solar spectra but corrode when dipped in electrolyte [14,15]. Intermediate band gap semiconductor like Fe_2O_3 absorbs in the visible region but suffer from poor semiconductor characteristics due to redox level mismatch, low mobility of holes and trapping of electrons by oxygen-deficient iron sites. In order to improve the lifetime of PEC system, the semiconductor material must have adequate electrochemical stability so that the charge carriers reaching at its surface drive only the water splitting reactions without any side reactions (i.e. electrode corrosion). Semiconductor materials are found to be more resistant to reduction reactions than that of oxidation reactions, which makes p-type material more suitable than n-type material with respect to stability. Alternatively, the thermodynamic

instability of photo-electrodes is due to the ability of photo-generated holes to oxidize the semiconductor [16].

Recently, $BiVO_4$ doped with Mo and W have shown very high catalytic activity. It was shown that appropriate W or Mo doping conditions would lead to much higher photocurrent generation activity and water photo-oxidation [17].

In addition, high cost and life time are the major challenges which need to be taken care of. Recently Cu_2WS_4 has been proposed which can play a role for PEC water splitting[18]. Cu_2WS_4 is a semiconductor with a band gap of approximately 2.0 eV and includes two species which are members of so called d-electron systems i.e. Cu $(Ar3d^{10}4s^1)$ and W $(Xe4f^{14}5d^46s^2)$. Usually d-electron system show strongly correlated behavior and theoretically utmost care is required to deal with such systems. In the present work, we have studied the ground state properties like lattice parameters and band-gap determination as well as absorption spectra within the UV-visible range.

CALCULATIONS

The electronic structure of $I-Cu_2WS_4$ was studied within density functional theory formalism. To calculate the electronic structure and lattice parameters of Cu_2WS_4, we have used full-potential linear augmented plane-wave (FLAPW) method as implemented in the WIEN2k code [19-21]. We have applied a recently developed approach in which a small component of exact exchange (which we will refer to as α) has to be added for the relevant Kohn–Sham orbitals (d-electrons only here), which can be calculated rather simply within the muffin tin of an APW method. This is similar to a LDA/GGA + U method, but with a U value that will vary with local environment avoiding the need to tune U for specific cases. Recently Cu_2WS_4 has been studied by BP86 functional [22] incorporated in ORCA code [23] for structural properties.

The value of α for a particular system can be tuned, i.e. a compromise can be used. The value of $\alpha = 0.6$ with the PBE functional gives the better results as far as the band gap determination is concerned, but at the same time lattice parameters deviate from the experimental values with considerable extent. Therefore a value $\alpha = 0.4$, would have been used for Cu_2WS_4 which gives better comparison for both band gap as well as lattice parameters. The band structure and partial density of states were calculated and compared for analysis.

Based on the structure and atomic arrangements, Cu_2WS_4 can have two lattice structures which are named as $p-Cu_2WS_4$, and $I-Cu_2WS_4$. In the P polymorph the molybdenum atoms in adjacent layers are located directly above each other, giving a lattice with primitive centring. In the I polymorph, the molybdenum atoms in adjacent layers are offset by half a unit cell in the a- and b-directions; molybdenum atoms in one layer lie above a metal vacancy in the next layer, presumably minimizing unfavorable electrostatic interactions. Basically, $I-Cu_2WS_4$ is fabricated by $Cu-S_4$ and $W-S_4$ tetrahedral units. **Fig.1** shows the atomic structure of Cu_2WS_4 decahedron viewed from arbitrary direction. It is obvious that it contains broken $Cu-S_4$ or $W-S_4$ tetrahedrons. **Fig. 2** shows the Density of States (DOS). It is evident that valance band composed of S 3p and Cu 3d orbits, whereas S 3p, W 5d, Cu 3d orbits constituted the conduction band. In addition, absorption spectra have been calculated which is shown in **Fig. 3.**
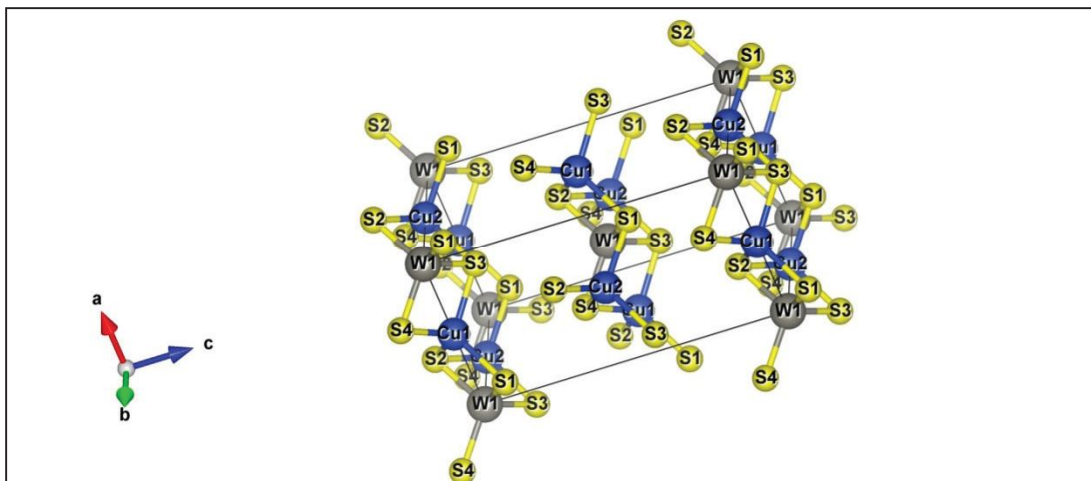
Figure 1: Lattice structure of Cu_2WS_4

RESULTS AND DISCUSSIONS

Evans *et. al.* had synthesized and determined the structural characterization of body centred polymorph of Cu_2WS_4 prepared using hydro thermal methods. I-Cu_2WS_4 crystallizes in space group I-42m with experimental cell parameters a=b=5.440 Å, c=10.07Å and has new structure type containing layers of edge-sharing CuS_4 and WS_4tetrahadra. The structure of $Cu_2WS_4$was determined by powder X-Ray diffraction data [24]. Gan and Schwingenschlogl studied two-dimensional mono-layers and nano-ribbons, they found the little smaller band gap values than the present study [25].

The purpose of using present proposed technique is to get results of lattice parameters and band gap with a balance between both computational and experimental values. For this purpose, we have done calculations with GGA and value of $\alpha = 0.4$ with the PBE functional and compared the results given by these two approximations. Using value of $\alpha = 0.4$ with the PBE functional gives lattice parameters with space group I-42m with cell parameters a=b=5.510 Å, c=10.110Åwhich does not deviate much from the experimental values.
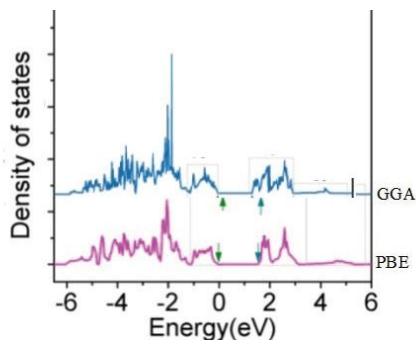

Figure 2: Comparison of Density of States calculated by GGA and PBE (+α) functional

A trend has been observed in which the bandgap increases with increase in the value of α. The optimized volume and lattice parameters decrease with increase in the value of α. Therefore the value of α can be chosen such that the balance can be maintained between both the lattice parameters calculations and bandgap determination.

Therefore a value $\alpha = 0.4$, would have been used for Cu_2WS_4 which gives better comparison for both band gap and lattice parameters. The calculated structure has been shown in **Fig.1**. **Fig. 2** shows the partial density of states of Cu_2WS_4 using GGA approximation which gives the band gap about 1.4 eV. From fig. 3, it is clear that W is contributing mainly in absorption.
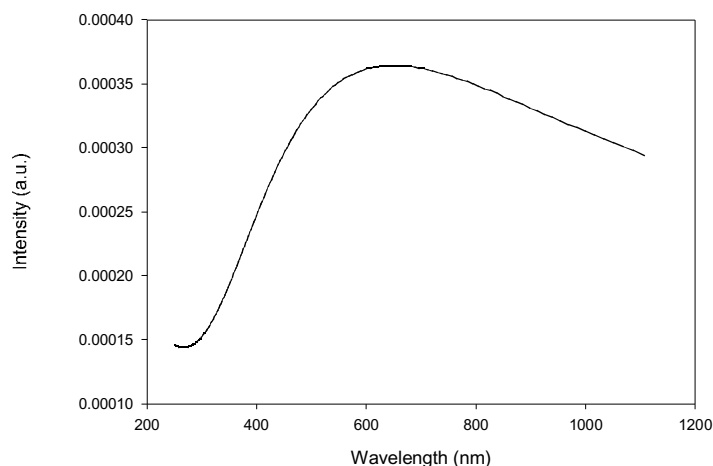
Figure 3: Absorption spectra of Cu₂WS₄

It is clear that band gap increases compared to GGA functional and comes out to be 1.8 eV. But we need to make a lot of compromise with lattice parameters. We have also tried with increased value of $\alpha = 0.6$ with the PBE functional to improve the value of bandgap towards experimental value. The value of bandgap improves and comes equal to experimental values 2.0 eV, but $\alpha = 0.6$ with the PBE functional takes the lattice parameters far away from the experimental values. Therefore value of $\alpha = 0.4$ with the PBE functional is an appropriate value for Cu_2WS_4, which makes a balance between lattice parameters and bandgap.

Cu_2WS_4 has been proposed to play role for PEC water splitting [18]. To split water, 1.7 eV potential is required which comes under the UV-visible region of light spectrum. Cu_2WS_4 is able to generate sufficient photo-voltage to split water into hydrogen and oxygen. It can be seen through the absorption spectra computed and shown in **Fig. 2** which is equivalent to bandgap of 1.8 eV.

CONCLUSIONS

In the present work, we have carried out Density Functional Study of Cu_2WS_4 using PBE functional with a small component of exact exchange (defined as α). In the present case $\alpha = 0.4$ has been found to be appropriate for the lattice structure calculation and band

structure calculation. This technique has given the results which are in good agreement with the experimental results. This technique requires very less computational resources compared to LDA/GGA + U or many-body perturbation theory (GW) approximation. For other materials "α" can be chosen in such way that results for both the lattice parameters and bandgap calculations can be determined without doing much compromise in comparison to the experimental values.

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