

# Combined theoretical and experimental study of the electronic and optical property of $\text{Sb}_2\text{WO}_6$

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## Abstract

Both theoretical and experimental analysis are carried out to understand the physical properties of the fascinating electronic and optical properties of antimony tungstate ( $\text{Sb}_2\text{WO}_6$ ). The nanosized ( $\sim 40 - 80 \text{ nm}$ ) material is produced using hydrothermal method followed by the SEM and XRD analysis to find the structural properties. The present calculations using PBEsol and PBE approximations for exchange-correlation potential are compared with the experimental structural parameters and in the case of the calculations using PBEsol approach the predicted crystal parameters and simulated XRD pattern are in excellent agreement with experimental results. The experimental absorption spectra measured in the ultraviolet-visible range give the bandgap of  $2.42 \text{ eV}$ , while the most intense peak of photoluminescence spectra is found at  $468 \text{ nm}$  ( $2.65 \text{ eV}$ ). Using density functional theory (DFT) technique, the band structure and density of states for  $\text{Sb}_2\text{WO}_6$  are calculated and the calculated bandgap of  $2.62 \text{ eV}$  is in agreement with the experimental finding. From theoretical partial density of states calculations we identify that the bandgap is formed between the  $\text{O}-2p_y$  orbitals bonded with Sb at valence band maxima and the  $\text{W}-5d_{x^2-y^2}$  orbital at conduction band minima. The atomic level transitions responsible for the peaks of absorption spectra and photoluminescence spectra are identified as well by the means of DFT calculations. Following the matching of theoretical and experimental observations, the calculations of optical properties reveal the plasma frequency to be equal to  $13.36 \text{ eV}$ .

## 1. Introduction

Within the semiconductor family oxides occupy a special place due to their exotic physical and chemical properties. The vibrancy of their characteristics is exhibited through Mott insulation [1], superconductivity [2], a high dielectric constant [3, 4], and excellent electrical, optical, as well as electrochromic characteristics [5]. The partially filled d-shells of transition metals play the key role in producing such different novel fascinating properties whereas, the hybridisation with oxygen p-electrons tunes it further. Tungsten trioxide ( $\text{WO}_3$ ) is such an example of semiconducting metal oxide exhibiting electrochromic property and various applications in field of gas sensing and other environmental remedies [5].

Metalloids, on the other hand, are p-elements in the Periodic Table often forming III-V semiconductors (e.g., GaAs, InSb). However, they often form oxides. Among others, oxides of Antimony also exhibit semiconductor properties, found in three distinct phases; antimony trioxide ( $\text{Sb}_2\text{O}_3$ ), antimony tetroxide ( $\text{Sb}_2\text{O}_4$ ), and antimony pentoxide ( $\text{Sb}_2\text{O}_5$ ) [6].

While oxides of both tungsten and antimony are promising materials for application, their bandgaps are wider

and fall under blue to ultraviolet (UV) region, e.g., the bandgap of  $\text{WO}_3$  is of the order of  $2.6 - 3.4 \text{ eV}$  [7, 8] and of  $\text{Sb}_2\text{O}_3$  is  $3.3 \text{ eV}$  [9]. Interestingly, though most of the tungstates are widegap materials ( $\text{Ag}_2\text{WO}_4 : 3.15 \text{ eV}$ ,  $\text{Bi}_2\text{WO}_6 : 2.8 \text{ eV}$ ),  $\text{Sb}_2\text{WO}_6$  is a relatively narrower bandgap candidate falling under visible region [10, 11].

Semiconductors with bandgap falling in visible range are of particular interest in photocatalytic application and optoelectronic device designing. Therefore, antimony tungstate,  $\text{Sb}_2\text{WO}_6$ , has attracted significant attention over recent decades.  $\text{Sb}_2\text{WO}_6$  is a member of the Aurivillius family represented by the general equation  $[\text{Sb}_2\text{O}_2][\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]$  of unique layered structure by perovskite slabs, where, the A and B are transition metal atoms with 6 and 12 coordination, respectively [12, 13, 14, 15]. Here m is the number of consecutive perovskite layers.  $\text{Bi}_2\text{WO}_6$  is one of the most renowned members of this family which is mostly used for the photocatalytic application for degradation of hazardous dyes in aqueous medium and hydrogen evolution by the decomposition of water [16, 17, 18].  $\text{Sb}_2\text{WO}_6$ , which is exhibiting its merit in similar field already, however, a detailed analysis on its characteristic features using coherent theoretical and experimental analysis is in due course. Theoretical understanding of the underlying mechanism governing the experimentally observed features of  $\text{Sb}_2\text{WO}_6$  should be helpful for further tuning of its properties which is yet

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to be explored. This study is an attempt to bridge the gap.

Here, we report a simple hydrothermal process of synthesizing  $\text{Sb}_2\text{WO}_6$ , followed by light absorption analysis in ultra-violet to visible (UV-Vis) region and photoluminescence spectral analysis. To understand the mechanism behind these physical properties, the density functional theoretical study has been carried out.

## 2. Methodology

### 2.1. Experimental Details

#### 2.1.1. Materials

All the chemicals are of analytical grade and used without further purification. Antimony Chloride ( $\text{SbCl}_3$ ) is purchased from Merck with 99.0% purity. Sodium Tungstate ( $\text{Na}_2\text{WO}_4$ ) is from Spectrochem Pvt. Ltd (India) with purity 99.0%. Deionised water (DI) is used for the synthesis purpose.

#### 2.1.2. Synthesis

Antimony Tungstate nanostructures are prepared using antimony chloride ( $\text{SbCl}_3$ ) and sodium tungstate ( $\text{Na}_2\text{WO}_4$ ) by the usual hydrothermal process [19]. Being a low cost, simple and easily controllable process, hydrothermal method is used for pure as well as doped and heterostructure sample preparation. The morphology and the average size of the nano particles can be controlled via tuning the temperature, time, sample concentration and pH of the solution.

Sodium tungstate and antimony chloride are dissolved in 22 ml DI water separately in 100 ml beakers followed by 15 minutes sonication and 30 minutes vigorous stirring. Sodium tungstate solution is then poured drop wise to the  $\text{SbCl}_3$  solution and kept for stirring during 1 hr to get a homogeneous mixture. After that the solution is transferred to the 55 ml teflon lined chamber in a steel autoclave at a temperature of  $180^\circ\text{C}$  for 12 hours. The solution is allowed to cool naturally and centrifuged several times with water-ethanol mixture to remove the unreacted salts. Finally, the product is dried at  $70^\circ\text{C}$  for overnight and collected by mortaring.

#### 2.1.3. Characterization

Structural characterization of the samples is carried out by using X-ray powder diffraction (XRD) measurements recorded using X-ray diffractometer (Model: Bruker AXS D8 Advanced) operating at 40 kV and 40 mA with  $\text{Cu-K}_\alpha$  radiation of  $1.5406\text{\AA}$ . XRD spectra are taken within  $2\theta$  range of  $15^\circ - 70^\circ$  using a scanning rate of  $0.003^\circ\text{s}^{-1}$ . The surface morphology of  $\text{Sb}_2\text{WO}_6$  is studied by ZESIS EVO 18 scanning electron microscopy (SEM). The UV-Vis spectrum is recorded in the absorbance mode in the wavelength range 200 nm to 800 nm by using the instrument Shimadzu UV-1800. Photoluminescence (PL) spectra of the samples are taken by using Horiba FL 1000 fluorescence spectrometer using 310 nm excitation.

### 2.2. Theoretical and Computational Methodology

For density functional calculations we use plane wave basis functional techniques as implemented in the Quantum Espresso (QE) code [20]. The ground state configurations are taken as:  $\text{Sb} \rightarrow 4d^{10}5s^25p^3$ ,  $\text{W} \rightarrow 5s^25p^65d^46s^2$ ,  $\text{O} \rightarrow 2s^22p^4$ . The structural relaxation is carried out to find energetically optimized cell using variable cell structural relaxation technique. Pseudopotentials appropriate for projected augmented wave (PAW) basis is used. We use Perdew-Burke-Ernzerhof (PBE) and the corrected form of PBE for solids (PBEsol) exchange-correlation potentials for structural analysis [21, 22]. The structural optimization is done with the maximum force of  $10^{-5}$  Ry./atom and pressure thresholds of  $10^{-5}$  kbar/cell. Fine  $6 \times 7 \times 4$  k-point grids ( $0.2/\text{\AA}$ ) is used and charge densities and energies are converged to  $10^{-8}$  Ry. We set kinetic-energy cut-off of 55 Ry and 500 Ry for the wavefunctions and charge densities, respectively. The simulated X-ray diffraction is produced using Vesta package [23]

As PBE or PBEsol approximations underestimate the bandgaps, so, we use Heyd-Scuseria-Ernzerhof (HSE06) screened hybrid functional for electronic and optical properties calculations [24]. The optimized norm-conserving Vanderbilt (ONCV) pseudopotentials are used for HSE calculations. The HSE06 band structure and density of states (DOS) are extracted using Wannier90 package [25]. For DOS calculation, adaptive smearing is utilised using denser  $25 \times 25 \times 25$  k-space grid.

For optical properties predictions, we calculate the complex dielectric tensor using random phase approximation (RPA).

$$\epsilon_{\alpha\beta}(\omega) = 1 + \frac{4\pi e^2}{\Omega N_{\mathbf{k}} m^2} \sum_{n,n'} \sum_{\mathbf{k}} \frac{\langle u_{\mathbf{k},n'} | \hat{\mathbf{p}}_\alpha | u_{\mathbf{k},n} \rangle \langle u_{\mathbf{k},n} | \hat{\mathbf{p}}_\beta^\dagger | u_{\mathbf{k},n'} \rangle}{(E_{\mathbf{k},n'} - E_{\mathbf{k},n})^2} \left[ \frac{f(E_{\mathbf{k},n})}{E_{\mathbf{k},n'} - E_{\mathbf{k},n} + (\hbar\omega + i\hbar\Gamma)} + \frac{f(E_{\mathbf{k},n})}{E_{\mathbf{k},n'} - E_{\mathbf{k},n} - (\hbar\omega + i\hbar\Gamma)} \right] \quad (1)$$

Here,  $\hat{\mathbf{p}}$  is the momentum operator,  $|u_{\mathbf{k},n}\rangle$  is the  $n$ -th state at  $\mathbf{k}$  point corresponding to the energy  $E_{\mathbf{k},n}$ ,  $\omega$  is the frequency of the incident photon,  $\Omega$  is the volume of the unit cell and  $N_{\mathbf{k}}$  is the number density of the charge carrier. Since no excited-state can have infinite lifetime, we introduce small inter-smearing  $\Gamma$  (0.2) in order to incorporate intrinsic broadening to all excited states. We calculate the imaginary part of the dielectric function  $\epsilon_{\alpha\beta}^{(i)}$  first, and, then the real part  $\epsilon_{\alpha\beta}^{(r)}$  using the Kramers-Kronig relation.

From  $\epsilon_{\alpha\beta}^{(r/i)}$  the optical conductivity, refractive index and

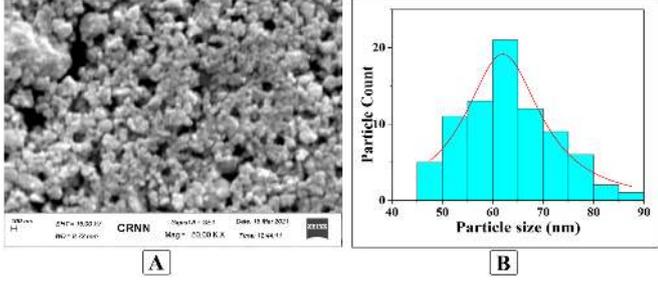


Figure 1: (A) SEM image of the  $\text{Sb}_2\text{WO}_6$  nanoparticles; (B) Particle size distribution obtained from the SEM image and fitted with Gaussian.

absorption coefficients can be found as [26]:

$$\text{Dielectric tensor: } \epsilon_{\alpha\beta} = \epsilon_{\alpha\beta}^{(r)} + i\epsilon_{\alpha\beta}^{(i)} \quad (2)$$

$$\text{Optical Conductivity: } \text{Re}[\sigma_{\alpha\beta}(\omega)] = \frac{\omega}{4\pi} \epsilon_{\alpha\beta}^{(i)}(\omega) \quad (3)$$

$$\text{Complex Refractive Index: } \mu_{\alpha\alpha} = n_{\alpha\alpha}^+ + in_{\alpha\alpha}^- \quad (4)$$

$$\text{Absorption Coefficient: } A_{\alpha\alpha}(\omega) = \frac{2\omega n_{\alpha\alpha}^-(\omega)}{c} \quad (5)$$

$$\text{where, } n_{\alpha\alpha}^{\pm}(\omega) = \sqrt{\frac{|\epsilon_{\alpha\alpha}(\omega)| \pm \epsilon_{\alpha\alpha}^{(r)}(\omega)}{2}}$$

### 3. Results and Discussions

#### 3.1. Structural Properties

##### 3.1.1. SEM Image

The surface morphology of the synthesized sample is studied using the SEM image. Fig.1(A) exhibits the shape and sizes of the sample particles as prepared. It is clear that the particles are very small spherical balls and are almost uniform in shape and the size of those fall within nanoregion. The distribution of the measured particle sizes of randomly selected 80 particles is presented by an histogram as shown in the Fig.1(B). The sample particles are found to be of 40 – 80 nm size, while, most probable particle size obtained by Gaussian fitting as 62 nm. Due to the small size of the particles, quantum confinement may give rise to the blue shifting of the bandgap.

##### 3.1.2. X-ray Diffraction Analysis

XRD technique is an effective tool to determine the phase, crystallinity and purity of the samples prepared. Fig.2(A) shows the XRD pattern of the synthesized  $\text{Sb}_2\text{WO}_6$  nanoparticles. The diffraction peaks at  $2\theta$  values of  $20.1^\circ$ ,  $27.0^\circ$ ,  $29.1^\circ$ ,  $32.9^\circ$ ,  $36.5^\circ$ ,  $40.3^\circ$ ,  $47.6^\circ$ ,  $49.9^\circ$ ,  $53.3^\circ$  and  $55.5^\circ$  correspond to the crystal planes with (hkl) values as shown in the Fig.2(A) [27]. These peaks correspond to the triclinic phase of  $\text{Sb}_2\text{WO}_6$  [JCPDS card no. 47-1680] [18]. The absence of no other peak confirms the pure phase formation of  $\text{Sb}_2\text{WO}_6$  crystal.

The broadening of the XRD pattern arises due to two reasons: finite size of the crystals and the strains developed in them. This strain arises due to formation of the defect in the crystal structure during synthesis as well as effect from grain boundaries. The Williamson-Hall (W-H) plot is a fruitful method to separate the broadening due to the above-mentioned two causes and also to determine the grain size of the crystal [30]. Accordingly, the total broadening  $\beta_{tot}$  of XRD peaks is equal to the sum of the broadening due to grain size ( $\beta_{size}$ ) and microstrain ( $\beta_{strain}$ ) developed in the crystal structure that can be written as

$$\beta_{tot} = \beta_{size} + \beta_{strain} \quad (6)$$

Using the crystalline size  $D$ , the microstrain  $\epsilon$  and the shape factor  $k = 0.9$  for spherical particles, the broadening due to crystal size and microstrain can be written as: Thus, the total strain:

$$\beta_{size} = \frac{k\lambda}{D\cos\theta}; \quad \beta_{strain} = 4\epsilon \tan\theta$$

$$\beta_{tot} = \frac{k\lambda}{D\cos\theta} + 4\epsilon \tan\theta \Rightarrow \beta_{tot} \cos\theta = \frac{k\lambda}{D} + 4\epsilon \sin\theta \quad (7)$$

In Fig.2(B), we present the W-H plot as calculated from the XRD pattern. From straight line fitting of the major peaks of the XRD pattern, we get the slope of the straight line is  $0.00168 \pm 0.00091$ . This is equal to the strain developed in the crystal. While the intercept of the straight line is  $0.00568 \pm 0.000668$  and the corresponding average grain size is 24.59 nm.

Using the initial input parameters provided by Ling *et al.* [12], the Rietveld analysis is done using FullProf software. The calculated lattice parameters as presented in Table 1 is similar to the previously reported values [12, 13]. The small deviation of angles  $\alpha$  and  $\gamma$  from  $90^\circ$  in all of these experiments suggest a triclinic phase of  $\text{Sb}_2\text{WO}_6$ .

##### 3.1.3. Theoretical Analysis

$\text{Sb}_2\text{WO}_6$  is a crystal which follows perovskite structure of layered Aurivillius phase [12, 13]. In Fig. 2(C) the unit cell of  $\text{Sb}_2\text{WO}_6$  is depicted. Each unit cell contains two formula units totalling 18 atoms. Sublayers are formed by  $\text{WO}_4$  (let say, A) and  $\text{Sb}_2\text{O}_2$  (B) in alternating ABAB... arrangement [31]. The  $2 \times 2 \times 2$  supercell of the structure clearly indicates the layered structure as seen in Fig.2(D). The arrangement of the  $\text{Sb}_2\text{O}_2$  sublayer follows a zigzag pattern resulting a lower symmetry of the crystal.

The lattice parameters found by our DFT study using PBE exchange-correlation functional are  $a = 5.641\text{\AA}$ ,  $b = 5.087\text{\AA}$  and  $c = 9.267\text{\AA}$ , while, the angles are  $90.00^\circ$ ,  $95.11^\circ$  and  $90.00^\circ$ . This is comparable with the experimental finding of Castro *et al.* ( $5.554\text{\AA}$ ,  $4.941\text{\AA}$ ,  $9.209\text{\AA}$ ;  $90.05^\circ$ ,  $96.98^\circ$ ,  $90.20^\circ$ ) [13]. The little overestimation of bond-lengths is an usual feature of PBE functional as it underbound atoms [22]. For a large set of semiconductors the mean of overestimation is calculated as 1.502% [32] and in  $\text{Sb}_2\text{WO}_6$  the mismatch is just 2.96%, 0.64%, 1.57%

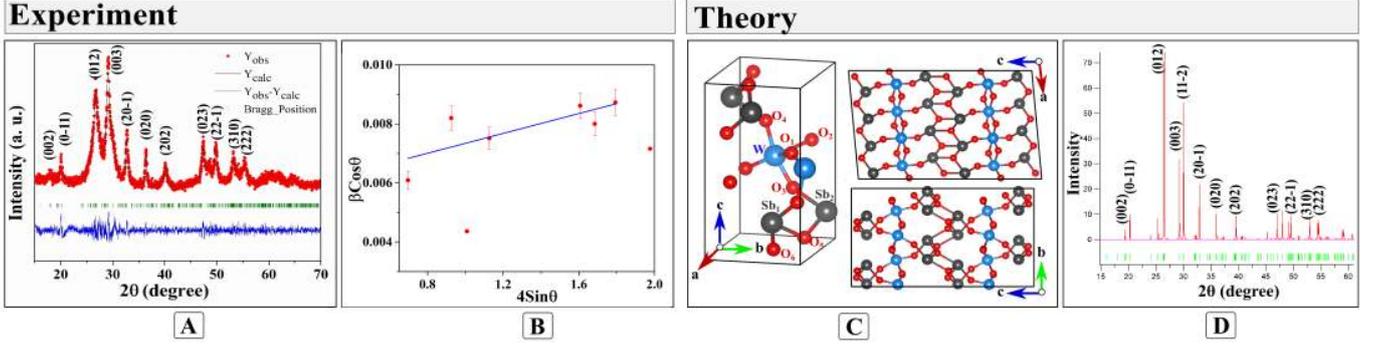


Figure 2: (A) The profile matching of XRD pattern of the  $\text{Sb}_2\text{WO}_6$  sample; (B)  $\beta\cos\theta$  versus  $4\sin\theta$  plot (W-H plot) and the straight line represents the average fitting; (C) Crystal structure and (D) Simulated X-ray diffraction pattern for  $\text{Sb}_2\text{WO}_6$ .

		Lattice Parameters						
	Formula Units	a (Å)	b (Å)	c (Å)	$\alpha$	$\beta$	$\gamma$	
Theo. (PBE)	2	5.641	5.087	9.267	90.00	95.11	90.00	
Theo. (PBEsol)	2	5.553	4.983	9.192	90.00	95.41	90.00	
Expt.	16	11.13	9.89	18.50	90.50	96.38	90.38	
Expt. [13]	2	5.554	4.941	9.209	90.05	96.98	90.20	
Expt. [12]	16	11.132	9.896	18.482	90.20	96.87	90.21	
		Band Gap (eV)						
	PBE	PBEsol	HSE06	Expt.	Theo. [28]	Expt. [29]	Expt. [18]	Expt. [16]
	1.78	1.35	2.62	2.42	2.91	2.30	2.46	2.17–2.63

Table 1: Lattice parameters and bandgap of  $\text{Sb}_2\text{WO}_6$  calculated using DFT methods compared with the experimental values obtained. Experimental lattice parameters of this study and that by Ling. *et al.* [12] are for  $2 \times 2 \times 2$  supercell.

for  $a, b, c$ , respectively. The W atom forms six W-O bonds among which four are almost planar in nature having O-W-O bond angles  $100.67^\circ, 87.11^\circ, 84.03^\circ, 88.17^\circ$ . The on plane W-O bond lengths are  $1.81\text{Å}, 2.12\text{Å}, 2.16\text{Å}, 1.80\text{Å}$  and the two out-of-the-plane bond lengths are  $1.89\text{Å}$ . So, we see that there is inherent asymmetry within the  $\text{WO}_4$  sublayer whereas the inter-sublayer ( $\text{Sb}_2\text{O}_2\text{-WO}_4$ ) region is maintaining a regularity.

On the other hand, PBEsol predicted structural parameters ( $5.553\text{Å}, 4.983\text{Å}, 9.192\text{Å}, 90.00^\circ, 95.41^\circ, 90.00^\circ$ ) are in excellent agreement with the experimental values when compared with PBE functional. This is because the slow varying density approximation is more accurate for any solid and in the PBEsol functional that is restored [22].

Though the lattice parameters calculated using PBEsol are almost similar to the experimental parameters found by Castro *et al.*, the mismatch of symmetry group is evident. While the experimental observation shows that  $\text{Sb}_2\text{WO}_6$  follows triclinic  $P1$  space group symmetry, the DFT calculations using both PBE and PBEsol indicate it as monoclinic ( $P2_1$ ) crystal. The  $\alpha$  and  $\gamma$  angles are found to be  $90^\circ$  using DFT calculations, whereas, the experimentally observed values deviate a little from  $90^\circ$  (see, Table 1). The deviation of the angles from a perfect  $90^\circ$  is responsible for the triclinic nature. However, Ling *et al.* have experimentally predicted the underlying monoclinic structure of  $\text{Sb}_2\text{WO}_6$  crystal [12]. For experimental ob-

servations, such variation is not rare as finite size effect is inevitable in experiments. For example, the lattice angle  $\beta$  of iron tungstate  $\text{FeWO}_4$ , which is found in  $P2/a$  symmetry, may vary from  $90.091^\circ$  to  $90.8^\circ$  [33, 34, 35]. Interestingly, the enantiomorphic nature (non-centrosymmetric) is predicted by both theoretical and experimental techniques.

The theoretically calculated XRD pattern is presented in Fig.2(D). The calculated peaks match well with the experimental observation. Unlike the experimental case, the calculated peaks are sharp and one can distinctly identify many of them. This is because the theoretical calculation is done on bulk material free from any size effect. The size effect makes the experimental XRD peaks blunt and, sometimes, less distinctly observable. Due to the broadening of the XRD peaks, the peak corresponding (11 - 2) is not visible in the experimental XRD. However, by deconvoluting the experimental XRD spectra between  $2\theta$  range  $28^\circ - 32^\circ$ , two peaks can be located. This is shown in Fig.6 of Appendix. The peak at  $29.25^\circ$  is due to (003) plane and peak at  $30.11^\circ$  is due to (11 - 2) plane.

### 3.2. Electronic and Optical Properties

#### 3.2.1. Ultraviolet-Visible Spectra

The optical property of the material is studied by UV-Vis absorbance spectroscopy. The absorption of photons energizes the electron to jump from valence band (VB)

to conduction band (CB), so, the absorption spectra provides the understanding of the electronic properties of the material concerned.

The observed UV-Vis spectra of the sample is shown in Fig.3(A). We can see from the figure there is a prominent absorbance ( $A$ ) of the material in the visible region. Following an almost flat region in  $\sim 200 - 208 \text{ nm}$  range, the absorbance start to increase and there is a peak observed at  $242 - 245 \text{ nm}$ . Beyond that the intensity starts to fall rapidly till  $450 \text{ nm}$  followed by a rather moderate fall till  $800 \text{ nm}$ .

Now, the absorbance is observed for a solution of  $\text{Sb}_2\text{WO}_6$ , so, the effect of the interaction between water and the sample surface on the spectra is unavoidable. Due to the interaction between water and the sample surface there is a little flatness in the absorbance spectra and very few prominent peaks are noticed. Similar nature of absorbance is observed in earlier works as well [27]. There is no sharp fall in absorbance near the bandgap energy attributing from this interaction as well. So, to detect the region of maximum change of absorbance we plot the  $\frac{dA}{d\lambda}$  versus wavelength  $\lambda$  as shown in Fig.3(B). The knee point of  $\frac{dA}{d\lambda}$ , where a straight-line fitting is done, can be identified as the point where the absorption just start increasing. The wavelength of this point should correspond the bandgap energy which is estimated as  $2.42 \text{ eV}$ .

### 3.2.2. Photoluminescence Spectra

In general, the recombination of photo-generated charge carriers can release energy for the emission of photoluminescence. The higher the PL intensity, higher the recombination of charge carriers and more the sample acts like fluorescent material. Fig.3(C) shows the photoluminescence spectra of antimony tungstate with the excitation of  $310 \text{ nm}$ . There is a prominent part of the emission in the visible region.

The most intense peak at  $468 \text{ nm}$  is attributed to the intrinsic luminescence of  $\text{Sb}_2\text{WO}_6$  [29]. The approximate bandgap energy as calculated from this peak corresponding to the PL spectra is  $2.65 \text{ eV}$ . From the theoretical partial DOS (PDOS) calculation discussed in the next subsection, we can identify that the peak originates from the electron transitions between the hybridized  $\text{Sb}-5s$  orbital and  $\text{O}-2p$  orbital lying in the VB and  $\text{W}-5d_{x^2-y^2}$  orbital in the CB [36, 37]. The peak at  $438 \text{ nm}$  may be formed due to the defect of the metal atoms and the oxygen vacancies produced during the crystal growth [36].

### 3.2.3. Band Structure and Density of State

The electronic structural analysis provides the understanding of the optical performance of materials, hence we investigate the energy band structure and DOS of the optimised structure. Both the PBE and PBEsol generalised gradient approximations (GGA) perform well for structural analysis, however, they underestimate the bandgaps of the semiconductors and insulators. The derivative discontinuity effect can not be properly addressed within such

non-empirical semi-local approximated schemes [38, 32]. The Hartree-Fock (H-F) approximation is a non-local exchange scheme and self-interaction free, so, in hybrid functional schemes a portion of H-F exchange is added. The HSE06 screened hybrid method is one of the best performing technique for proper bandgap prediction and is computationally less demanding than the density functional perturbative theoretical approximations ( $GW$  based quasiparticle methods) [39]. We use HSE06 hybrid functional for electronic structural calculations as well as for optical property prediction [24].

In Fig.3(D), the energy band dispersion and DOS using HSE06 is depicted. The coordinates of high symmetry points can be found in Table .3 of Appendix. The bandgap is estimated as  $2.62 \text{ eV}$ . The valence band maxima (VBM) is located at  $\Gamma$  point and the conduction band minima (CBM) is at  $B$  point, hence the bandgap is indirect in nature. From Table 1, we see that the bandgap is within the range of experimentally observed values. The energy band dispersion near the CBM is flat along the  $\Gamma - B$  line. Due to this flatness of the band there is a small peak of DOS at CBM denoted by  $C_1$ . There is a degeneracy of two bands along the  $E - Z - C_2$  and  $Z - D$  segments of irreducible Brillouin zone (BZ) in both of lowest lying conduction and highest lying valence band region. The almost separate two bands just below VBM is the reason of the sharp  $V_2$  peak. The overlap of bands for a large region of BZ indicates strong hybridization. Similar degeneracy is observed for the next two bands in VB. It is interesting that the band degeneracies do not appear near the BZ centre  $\Gamma$ . While there are a series of distinct sharp peaks of DOS in CB denoted by  $C_2, C_3, C_4 \dots$ , the DOS in VB is comprised of small peaks ( $V_1, V_3, V_4, \dots$ ) except the tall sharp peak  $V_2$  discussed above.

The origin of the energy bands can be understood using the atomic orbital projected DOS. In Fig.4(A) we present the PDOS for Sb, W and O atoms. If we look back to the crystal structure in Fig.2(C), we see that the  $\text{Sb}_1$  and  $\text{Sb}_2$  atoms produce bonding with  $\text{O}_5$  and  $\text{O}_6$ . The PDOS plots suggest hybridization of  $\text{Sb}-5s$  with  $\text{O}_5 - 2p_y$  and  $\text{O}_6 - 2p_y$  near the VBM level, with a small contribution from  $\text{Sb}-5p_y$ , corresponding  $V_1$  and  $V_2$  peaks in Fig.3(D). The  $V_5$  and  $V_6$  peaks are originating from oxygen  $2p$  levels; mainly the  $2p_z$  orbital of  $\text{O}_1$  and  $\text{O}_2$ , and,  $2p_x$  orbital of  $\text{O}_3$  and  $\text{O}_4$  produce the sharpness. Especially  $\text{O}_4 - 2p_x$  PDOS is distinctly sharp. CB is populated by  $\text{W}-5d$  orbitals producing the spaghetti of sharp peaks of DOS. Near the CBM contribution is coming mostly from  $\text{W}-5d_{x^2-y^2}$  orbital, with small contribution from the  $2p$  orbitals of surrounded  $\text{O}_1$  to  $\text{O}_4$  atoms. Hence, the PDOS plot in Fig.4 demonstrates that  $\text{O}-2p$  states are principal contributors to the upper portion of the valence band and  $\text{W}-5d$  states give the main input in the lower portion of the valence band. On the other hand, the conduction band is dominated by unoccupied  $\text{W}-5d$  states. It is worth mentioning that, the same feature regarding occupation of the valence band and conduction band regions by  $\text{O}-2p$  and

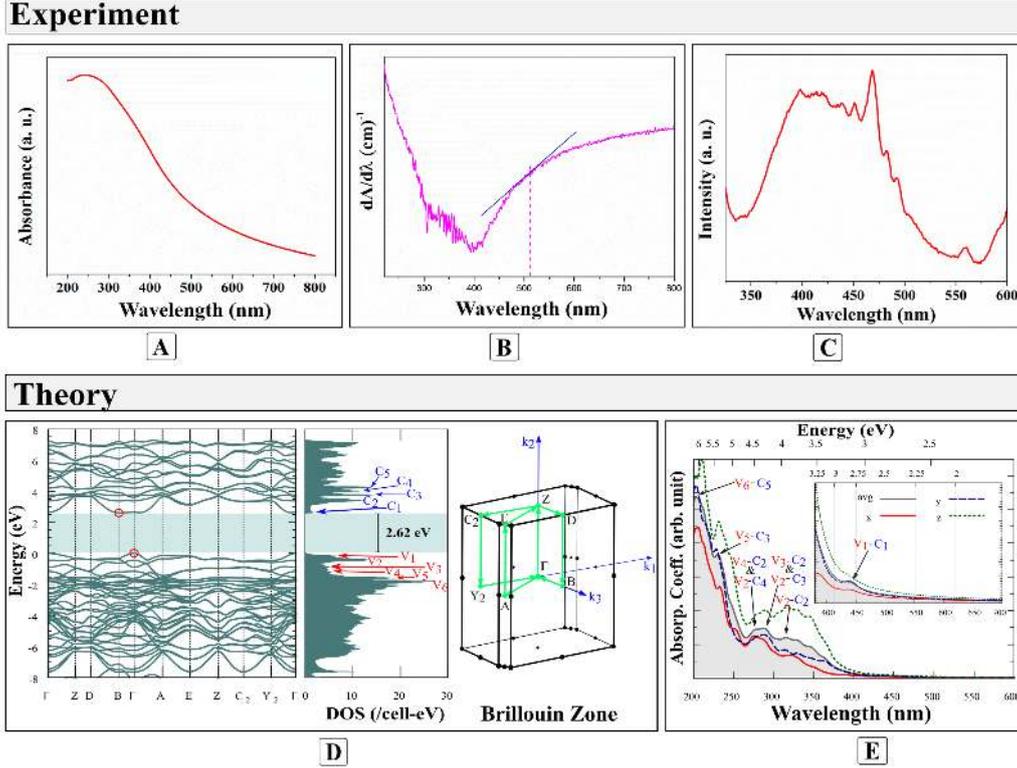


Figure 3: (A) UV-Vis absorbance spectra in water solution; (B) The  $\frac{dA}{d\lambda}$  versus wavelength plot; (C) Photoluminescence spectra of the antimony tungstate; (D) Energy band structure and density of states and (E) Absorption Coefficient calculated using HSE06 hybrid functional for  $\text{Sb}_2\text{WO}_6$ .

$W-5d$  states was found to be characteristic of other related tungstates with the common formula  $\text{MWO}_4$  ( $M = \text{Fe, Co, Cu, Zn, Cd}$ ) [40, 41, 33, 42].

To be more specific about the atomic contribution at VBM and CBM, we calculate the band projected charge density at the VBM for  $\Gamma$  point and at CBM for  $B$  point. This plot is similar to the wannier orbital plot as the charge density is basically the squared value of the wavefunction. The plots presented in Fig.4(B) confirm that the bandgap is between the  $O_5 - 2p_y$  and  $O_6 - 2p_y$  at VBM and  $W-5d_{x^2-y^2}$  at CBM. Small contributions from  $O_1$  and  $O_2$  at CBM is evident in the figure indicating the hybridization. When we perform the wannierization to find maximally localised Wannier functions (MLWF) we find that the Wannier centres are shifted from the atom centres, which confirms the hybridization of orbitals.

The atomic bonding nature can be qualitatively understood using Bader charge transfer analysis [43]. The calculated transferred charges for the atoms are presented in Table 2. It shows that the polyhedra formed by W atom surrounded by  $O_1$  to  $O_4$  atoms has a net charge of  $-1.75$  and  $\text{Sb}_2\text{O}_2$  have a net charge of  $1.75$ . So, we can conclude that there is a net charge transfer from the  $\text{Sb}_2\text{O}_2$  sublayer to  $\text{WO}_4$  sublayer producing an ionic bonding between these two sublayers. The total charge density plot in Fig.4(B) also indicates the ionic bonding nature as the

Atom	Charge
$\text{Sb}_1$	1.82
$\text{Sb}_2$	1.83
W	2.43
$O_1$	-0.87
$O_2$	-0.89
$O_3$	-1.03
$O_4$	-1.03
$O_5$	-1.14
$O_6$	-1.13

Table 2: Bader charge transfer.

charges around the atoms are almost spherically symmetric.

So, we identify the origin of the bandgap as well as the nature of atomic bonding from the DFT study. Also, the calculated gap comes in good agreement with that found from PL spectra. Motivated by such excellent agreement between the theoretical and experimental observations, we do further theoretical calculations on the optical properties.

### 3.2.4. Absorption Coefficient

As HSE06 functional can estimate the bandgap almost exactly, so, we further use it for the calculation of opti-

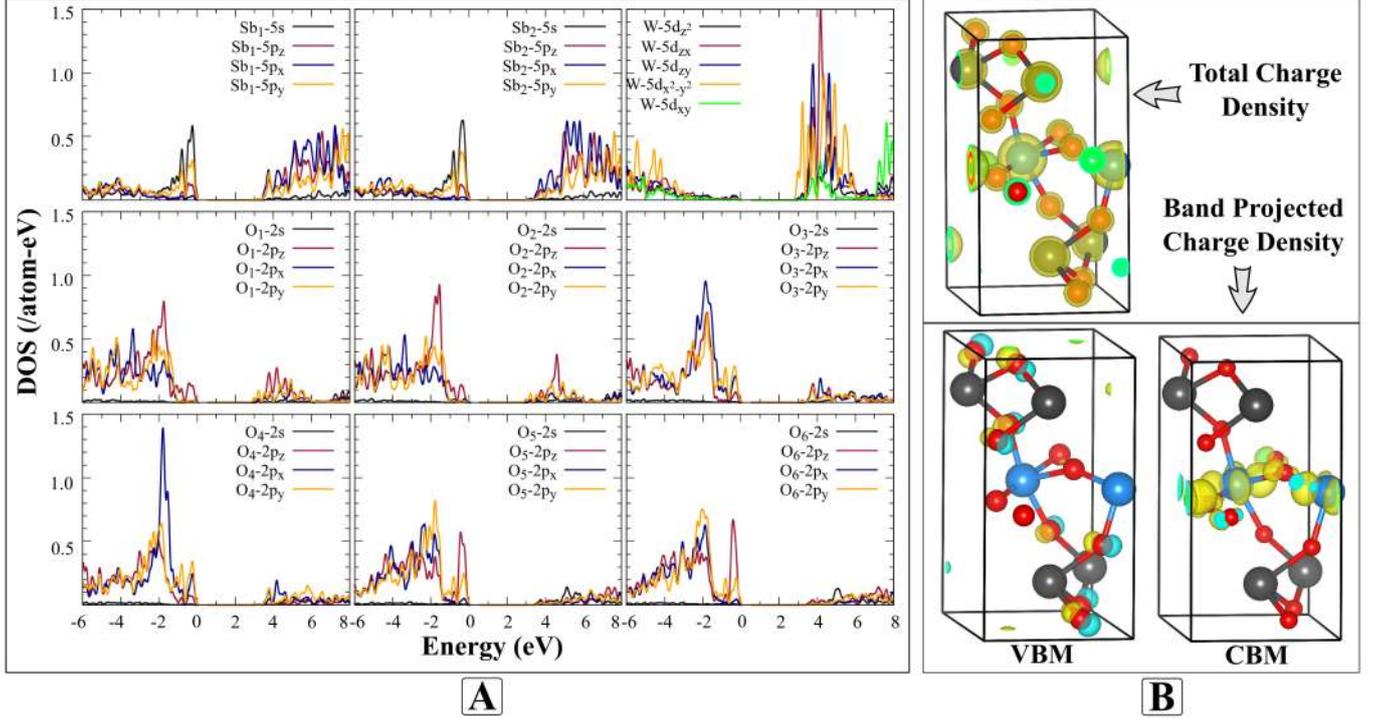


Figure 4: (A) Atomic orbital projected DOS of Sb<sub>2</sub>WO<sub>6</sub>; (B) Total charge density and the charge densities for VBM and CBM at the  $\Gamma$  and B points, respectively.

cal properties which are directly related to the electronic structure of materials. The jump of electron from a state to another is the mechanism behind the optical response; in metals both of inter-band and intra-band transitions are important, whereas, in gapped systems the optical response is dominated by inter-band leap. Ideally, a photon with a minimum of bandgap energy is required to move an electron from VB to CB producing a hole in the VB. Photons with higher energy than bandgap initiates the transition to higher level of conduction band, hence, in optical response calculations a plenty of empty conduction bands are thus necessary to be taken into consideration. In VB region, the number of available electrons for the inter-band transitions is expressed in term of effective electron number ( $n_{eff}$ ) as:

$$n_{eff}(E_m) = \frac{2m}{Ne^2h^2} \int_0^{E_m} E \cdot \epsilon_{\alpha\alpha}^{(i)}(E) dE; \quad (8)$$

Here,  $m$ ,  $e$  and  $N$  are electronic mass, charge and number density. Calculation reveals that the electrons below 15 eV from VBM cannot contributing in the optical transitions. As a consequence, 0 – 15 eV range is a optimal choice of optical property calculations.

The absorption coefficient as calculated using Eq.5 is presented in Fig.3(E); on the shaded region of total absorption, the individual components are depicted as well. All the other optical properties are discussed in the following section, here we try to compare the experimental and

theoretical absorption results side by side to get an insight on the underlying physical phenomena.

Similar to the experimental observation, there is a small peak near 200 nm. The sharp fall following that is also evident, however, in theoretical calculation the fall is stiffer than the experimental one. The fall goes on till  $\sim 265$  nm and thereafter a plateau is seen with almost flat top in  $\sim 275 - 290$  nm region. Following that, the fall is gradual and there is no absorption after  $\sim 475$  nm. The calculated bandgap is 2.62 eV corresponding 473.22 nm, so, there should not be any absorption beyond that. As, comparing to the higher energy region the absorption in visible light region ( $\sim 380 - 700$  nm) is quite low, so, we magnify the plot in the inset for this region. The energy corresponding to the wavelength range is also depicted on the upper x-axis, in both of the plots.

Now, let us investigate the origin of the peaks in the absorption coefficient plots starting from lower energy towards higher energy (higher to lower wavelength) i.e., from right to left of Fig.3(E). The first distinct peak is at  $\sim 2.8$  eV (see, inset) corresponding to the  $V_1 - C_1$  transition. The transition between the first two sharp peaks  $V_2 - C_2$  is seen around 3.9 eV. The next two peaks indicated in the figure are higher than the surroundings due to two transitions for each one. As there is a sharp rise of DOS from  $V_4$  to  $V_5$ , the absorption coefficient rises sharply till 5.38 eV corresponding  $V_5 - C_3$  peak, and the next peak is near 200 nm ( $\sim 6$  eV) is due to the  $V_6 - C_5$  transition.

Along with these indicated peaks, it is expected to have a distinct  $V_2 - C_5$  transition peak at  $\sim 4.7$  eV, however, there is none. When minutely investigated, we note that the valley between  $C_3 - C_4$  and  $V_2 - V_3$  have a gap of  $\sim 4.7$  eV as well, so, we conclude that in the backdrop of this the expected  $V_2 - C_5$  is absent.

We have discussed the similarities of the experimental and theoretical absorption spectra, however, we should note the difference of those as well. The DFT calculation is on the bulk, whereas, the experimental observation is on nano sized materials. The surface effect for small sized particles play significant role in optical absorption. Furthermore, there are interactions between water and the sample and the effect of the solvent water molecules makes the experimental spectra smoother. Though in theoretical calculation there should not be any absorption below the bandgap of the material, the scenario of experimental setup is quite different. We observe very low, but not tending to zero, absorption below the bandgap energy and the surface effect as well as the solvent environment is the reason behind such usual behaviour in experiments.

### 3.2.5. Other Optical Properties

We see that by proper choice of DFT method, one can find excellent agreement of the structural and electronic properties as well as can dig out the atomic level reasoning behind the experimentally observed photoluminescence and absorption profile. Such understanding let us move further to the theoretical studies on other optical properties. The calculation method is straight forward as discussed in the Methodology section.

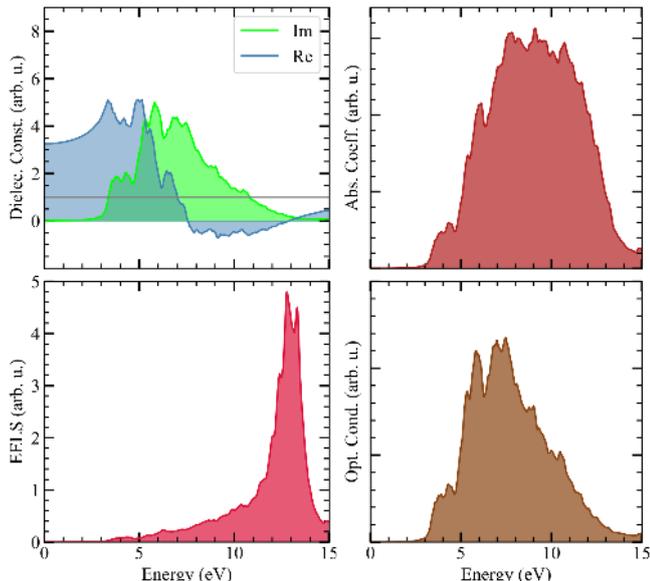


Figure 5: Theoretically calculated dielectric constant, electron energy loss spectrum, absorption coefficient and optical conductivity of  $Sb_2WO_6$ .

In Fig.5 we plot the dielectric constant, electron energy

loss spectrum (EELS), absorption coefficient ( $A$ ) and optical conductivity ( $\sigma$ ) of  $Sb_2WO_6$ . The imaginary part of dielectric constant  $\epsilon^{(i)}$  remains zero till the bandgap energy. It then starts to rise rapidly till reaching a small flat peak region 3.5 eV before it restarts its climb again. Near 5.5 eV the  $\epsilon^{(r)}$  becomes higher than  $\epsilon^{(i)}$ . The plasma frequency is defined as the frequency when  $\epsilon^{(r)}$  crosses the zero axis going from negative to positive value while having  $\epsilon^{(i)} < 1$  which is calculated as 13.36 eV.

The plasma frequency can be readily verified from the distinct peak in EELS. The EELS is seen as a sharply peaked spectrum with very low value below 10 eV. High value of plasma frequency is a signature character of most of the semiconductors,  $Sb_2WO_6$  is not an exception in that sense.

The same absorption coefficient presented in Fig.3(E) is now plotted for a wider range of energy, here, in this figure. We see that beyond the 6.2 eV energy corresponding to the 200 nm, the absorption coefficient rises further and exhibits an almost bell shaped nature. The highest range of absorption is in 7.2 – 11 eV range. This is because of the highest range of DOS in VB, with peak at  $V_6$  and fall  $\sim -7$  eV with respect to the VBM (see, Fig.3(D)).

The optical conductivity is directly related to the imaginary part of the dielectric constant through Eq.3. In Fig.5 such correspondence is readily visible. Now, absorption of photonic energy to produce electron-hole combinations is represented in absorption coefficient while the optical conductivity is the representative of the conducting property of the same electron-hole pairs. As larger number of electrons moves to CB through photon absorption, the carrier concentration also increases which reflects in higher optical conductivity. This signature is also evident from the plots. The conductivity jumps up just above the bandgap value (2.62 eV), and, even below 5 eV the optical conductivity is not very low. The flatness of the bands in the vicinity of VBM and CBM makes the conductivity profile almost flat for  $\sim 2.6 - 4.9$  eV. Beyond that the sharp increase follows the profile of absorption spectra.

## 4. Conclusion

We provide a combined theoretical and experimental study on  $Sb_2WO_6$  exhibiting its merit. The sample is produced using hydrothermal procedure. The XRD measurement proves its purity, whereas, the W-H plot and SEM measurements show that the particle size is of the order of 40 – 80 nm. The peaks of the simulated XRD pattern for  $Sb_2WO_6$  match well with the experimental observation. The UV-Vis absorption spectra shows similar pattern as the DFT calculated one. From UV-Vis spectra the bandgap is found as 2.42 eV, whereas, the bandgap calculated using HSE06 functional (2.62 eV) falls within the range found in experiments. Thus with the help of energy band diagram and atomic orbital projected DOS we can identify the transitions responsible for the particular nature of the absorbance experienced experimentally. The

origin of the bandgap is identified as the energy difference between states occupied by the  $O-2p_y$  orbitals bonded with the Sb atom at VBM, and, the  $W-5d_{x^2-y^2}$  orbital at CBM. From the PDOS plot, the peak of PL spectra at 468 nm (2.65 eV) can be associated with the transition between hybridized  $Sb-5s$ ,  $O-2p$  at VB and  $W-5d$  at CB. The significantly higher plasma frequency calculated for  $Sb_2WO_6$  (13.36 eV) is the character of semiconductors. So, our attempt of understanding the underlying physics of experimentally promising  $Sb_2WO_6$  paves the way for further tuning of its optical and electronic properties as well as establishes the importance of synchronization of experimental and theoretical works.

### Credit Author Statement

The experimental characterisation and analysis are done by D. Karmakar and D. Jana and the theoretical analysis is done by S. Datta. With the contribution of D. Karmakar and D. Jana in experimental section, the manuscript is mainly developed by S. Datta. D. Karmakar and S. Datta contribute equally to this study.

### References

### References

- [1] H. Watanabe, T. Shirakawa, S. Yunoki, Microscopic study of a spin-orbit-induced mott insulator in ir oxides, *Physical Review Letters* 105 (21) (2010) 216410.
- [2] Z.-X. Shen, D. S. Dessau, Electronic structure and photoemission studies of late transition-metal oxides—mott insulators and high-temperature superconductors, *Physics Reports* 253 (1-3) (1995) 1–162.
- [3] J. Robertson, High dielectric constant gate oxides for metal oxide si transistors, *Reports on Progress in Physics* 69 (2) (2005) 327.
- [4] C. Homes, T. Vogt, S. Shapiro, S. Wakimoto, A. Ramirez, Optical response of high-dielectric-constant perovskite-related oxide, *Science* 293 (5530) (2001) 673–676.
- [5] V. R. Buch, A. K. Chawla, S. K. Rawal, Review on electrochromic property for  $wo_3$  thin films using different deposition techniques, *Materials Today: Proceedings* 3 (6) (2016) 1429–1437.
- [6] H. S. Chin, K. Y. Cheong, K. A. Razak, Review on oxides of antimony nanoparticles: synthesis, properties, and applications, *Journal of Materials Science* 45 (22) (2010) 5993–6008.
- [7] P. González-Borrero, F. Sato, A. Medina, M. L. Baesso, A. C. Bento, G. Baldissera, C. Persson, G. A. Niklasson, C. G. Granqvist, A. Ferreira da Silva, Optical band-gap determination of nanostructured  $wo_3$  film, *Applied Physics Letters* 96 (6) (2010) 061909.
- [8] S. Deb, Optical and photoelectric properties and colour centres in thin films of tungsten oxide, *Philosophical Magazine* 27 (4) (1973) 801–822.
- [9] Z. Deng, F. Tang, D. Chen, X. Meng, L. Cao, B. Zou, A simple solution route to single-crystalline  $sb_2o_3$  nanowires with rectangular cross sections, *The Journal of Physical Chemistry B* 110 (37) (2006) 18225–18230.
- [10] B. Zhu, P. Xia, Y. Li, W. Ho, J. Yu, Fabrication and photocatalytic activity enhanced mechanism of direct z-scheme  $g-C_3N_4/Ag_2WO_4$  photocatalyst, *Applied Surface Science* 391 (2017) 175–183.
- [11] L. Zhang, H. Wang, Z. Chen, P. K. Wong, J. Liu,  $Bi_2WO_6$  micro/nano-structures: synthesis, modifications and visible-light-driven photocatalytic applications, *Applied Catalysis B: Environmental* 106 (1-2) (2011) 1–13.
- [12] C. D. Ling, R. Withers, A. D. Rae, S. Schmid, J. G. Thompson, Antiferroelectric modulations in  $Sb_2WO_6$  and  $Sb_2MoO_6$ , *Acta Crystallographica Section B: Structural Science* 52 (4) (1996) 610–615.
- [13] A. Castro, P. Millan, R. Enjalbert, E. Snoeck, J. Galy, An original oxide of antimony and tungsten related to aurivillius phases, *Materials Research Bulletin* 29 (8) (1994) 871–879.
- [14] A. Castro, P. Millan, R. Enjalbert, Structural evolution of the aurivillius framework in the solid solutions  $bi_2wo_6-sb_2wo_6$ , *Materials Research Bulletin* 30 (7) (1995) 871–882.
- [15] A. Castro, R. Enjalbert, J. Galy,  $Sb_2MoO_6$ , a re-examination, *Acta Crystallographica Section C: Crystal Structure Communications* 53 (11) (1997) 1526–1529.
- [16] C. Yang, X. Yang, F. Li, T. Li, W. Cao, Controlled synthesis of hierarchical flower-like  $sb_2wo_6$  microspheres: Photocatalytic and superhydrophobic property, *Journal of Industrial and Engineering Chemistry* 39 (2016) 93–100.
- [17] Z. J. Zhang, X. Y. Chen,  $Sb_2MoO_6$ ,  $Bi_2MoO_6$ ,  $Sb_2WO_6$ , and  $Bi_2WO_6$  flake-like crystals: Generalized hydrothermal synthesis and the applications of  $Bi_2WO_6$  and  $Bi_2MoO_6$  as red phosphors doped with  $Eu^{3+}$  ions, *Materials Science and Engineering: B* 209 (2016) 10–16.
- [18] S. Chen, M. Zhou, T. Li, W. Cao, Synthesis of ag-loaded  $Sb_2WO_6$  microsphere with enhanced photocatalytic ability for organic dyes degradations under different light irradiations, *Journal of Molecular Liquids* 272 (2018) 27–36.
- [19] A. Rabenau, The role of hydrothermal synthesis in preparative chemistry, *Angewandte Chemie International Edition in English* 24 (12) (1985) 1026–1040.
- [20] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. D. Corso, S. de Gironcoli, P. Delugas, R. A. DiStasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. O. de-la Roza, L. Paulatto, S. Poncè, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, S. Baroni, Advanced capabilities for materials modelling with quantum ESPRESSO, *Journal of Physics: Condensed Matter* 29 (46) (2017) 465901.
- [21] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Physical Review Letters* 77 (18) (1996) 3865.
- [22] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, K. Burke, Restoring the density-gradient expansion for exchange in solids and surfaces, *Physical Review Letters* 100 (13) (2008) 136406.
- [23] K. Momma, F. Izumi, Vesta 3 for three-dimensional visualization of crystal, volumetric and morphology data, *Journal of Applied Crystallography* 44 (6) (2011) 1272–1276.
- [24] J. Heyd, J. E. Peralta, G. E. Scuseria, R. L. Martin, Energy band gaps and lattice parameters evaluated with the heyd-scuseria-ernzerhof screened hybrid functional, *The Journal of Chemical Physics* 123 (17) (2005) 174101.
- [25] G. Pizzi, V. Vitale, R. Arita, S. Blügel, F. Freimuth, G. Géranton, M. Gibertini, D. Gresch, C. Johnson, T. Koretsune, et al., Wannier90 as a community code: new features and applications, *Journal of Physics: Condensed Matter* 32 (16) (2020) 165902.
- [26] F. Wooten, *Optical properties of solids*, Academic press, 2013.
- [27] C. Ding, Z. Li, W. Tan, H. Li, J. Ma, Z. Chen, Y. Tao, Y. Qin, Y. Kong, 3d graphene aerogels/ $Sb_2WO_6$  hybrid with enhanced photocatalytic activity under uv-and visible-light irradiation, *Synthetic Metals* 246 (2018) 137–143.
- [28] B. Huang, J. N. Hart, DFT study of various tungstates for

photocatalytic water splitting, *Physical Chemistry Chemical Physics* 22 (3) (2020) 1727–1737.

- [29] U. Rafiq, K. Majid, In situ growth of orthorhombic Sb<sub>2</sub>WO<sub>6</sub> hierarchical structures on reduced graphene oxide (rGO) sheets via solvothermal approach for superior and substantially improved visible-light driven photocatalytic activity, *Journal of Materials Science: Materials in Electronics* 30 (6) (2019) 5965–5977.
- [30] B. D. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley Publishing, 1956.
- [31] A. Ramirez, R. Enjalbert, J. Rojo, A. Castro, New aurivillius-related phases in the Sb-(W, V)-O system: structural study and properties, *Journal of Solid State Chemistry* 128 (1) (1997) 30–37.
- [32] S. Datta, D. Jana, *Semiconductor physics: A density functional journey* (arXiv:2010.13050) (2020). arXiv:2010.13050.
- [33] S. Rajagopal, V. Bekenev, D. Nataraj, D. Mangalaraj, O. Y. Khyzhun, Electronic structure of FeWO<sub>4</sub> and CoWO<sub>4</sub> tungstates: First-principles fp-lapw calculations and x-ray spectroscopy studies, *Journal of Alloys and Compounds* 496 (1-2) (2010) 61–68.
- [34] F. Yu, U. Schanz, E. Schmidbauer, Single crystal growth of FeWO<sub>4</sub> and CuWO<sub>4</sub>, *Journal of Crystal Growth* 132 (3-4) (1993) 606–608.
- [35] Y.-X. Zhou, H.-B. Yao, Q. Zhang, J.-Y. Gong, S.-J. Liu, S.-H. Yu, Hierarchical FeWO<sub>4</sub> microcrystals: solvothermal synthesis and their photocatalytic and magnetic properties, *Inorganic Chemistry* 48 (3) (2009) 1082–1090.
- [36] Q. Xiao, J. Zhang, C. Xiao, X. Tan, Photocatalytic degradation of methylene blue over Co<sub>3</sub>O<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub> composite under visible light irradiation, *Catalysis Communications* 9 (6) (2008) 1247–1253.
- [37] J. Li, Z. Guo, Z. Zhu, Ag/Bi<sub>2</sub>WO<sub>6</sub> plasmonic composites with enhanced visible photocatalytic activity, *Ceramics International* 40 (5) (2014) 6495–6501.
- [38] J. P. Perdew, R. G. Parr, M. Levy, J. L. Balduz, Density-functional theory for fractional particle number: Derivative discontinuities of the energy, *Physical Review Letters* 49 (1982) 1691–1694.
- [39] T. M. Henderson, J. Paier, G. E. Scuseria, Accurate treatment of solids with the HSE screened hybrid, *Physica Status Solidi (b)* 248 (4) (2011) 767–774.
- [40] O. Y. Khyzhun, V. Bekenev, Y. M. Solonin, First-principles calculations and x-ray spectroscopy studies of the electronic structure of CuWO<sub>4</sub>, *Journal of Alloys and Compounds* 480 (2) (2009) 184–189.
- [41] V. Atuchin, E. Galashov, O. Khyzhun, V. Bekenev, L. Pokrovsky, Y. A. Borovlev, V. Zhdankov, Low thermal gradient czochralski growth of large CdWO<sub>4</sub> crystals and electronic properties of (010) cleaved surface, *Journal of Solid State Chemistry* 236 (2016) 24–31.
- [42] O. Khyzhun, V. Bekenev, V. Atuchin, E. Galashov, V. Shlegel, Electronic properties of ZnWO<sub>4</sub> based on ab initio fp-lapw band-structure calculations and x-ray spectroscopy data, *Materials Chemistry and Physics* 140 (2-3) (2013) 588–595.
- [43] W. Tang, E. Sanville, G. Henkelman, A grid-based bader analysis algorithm without lattice bias, *Journal of Physics: Condensed Matter* 21 (8) (2009) 084204.

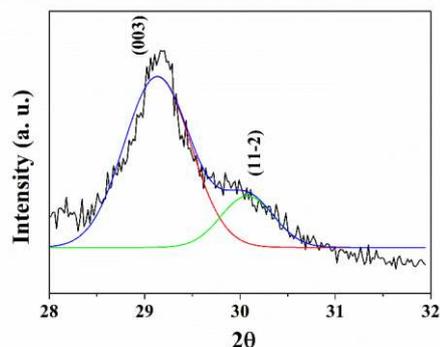


Figure .6: Deconvoluted XRD spectra between  $2\theta$  range  $28^\circ - 32^\circ$

Label	$k_1$	$k_2$	$k_3$
$\Gamma$	0.0	0.0	0.0
A	-0.5	0.0	0.5
B	0.0	0.0	0.5
$C_2$	-0.5	0.5	0.0
D	0.0	0.5	0.5
E	-0.5	0.5	0.5
$Y_2$	-0.5	0.0	0.0
Z	0.0	0.5	0.0

Table .3: High symmetry points of Brillouin zone.

## Appendix