Photocatalytic and photoelectro-chemical investigations of Fe/Sn/Nb containing oxides for energy application: Comparative study

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Abstract. The physico-chemical property of any bulk material is mainly determined by its lattice structure. To improve the understanding of opto-electronic response of any photocatalyst system, it is thus necessary to investigate the underlying physics of these materials. The world is exploring various metal-oxides to identify an efficient energy material, specifically with the interest towards solar energy conversion. The work discusses typical important example of ferrite, stannate and niobate containing photocatalyst systems; and compares their photocatalytic aspects for solar hydrogen production. Though ferrites and stannate are expected to be abundant eco-friendly systems, in contrast the niobates are highly efficient photocatalytic systems. Experimental results validate niobates as efficient system as compared to the ferrites/stannates. Computation using density functional theory demonstrates that in Fe-based oxides, d-orbital play a vital role to render visible light character, which is not the case in niobate like PbBi$_2$Nb$_2$O$_9$. The best suited band energetics w.r.t. redox levels of water splitting, yields high efficiency photocatalyst. The present work displays a direct correlation of experimental observations with computed results for the photocatalytic system those are used for solar energy conversion

1. Introduction

Energy crisis faced by mankind is demanding exploration of efficient energy generating materials by making use of the present day advanced tools of science. The physico-chemical property of any material system is mainly determined by its lattice structure, which in turns determines their optical, electrical and magnetic properties [1, 2]. The photocatalysts require certain stringent requirements with respect to the optical and electrical behavior of the constituent material. On one hand, it demands low band-gap material to absorb larger fraction of solar spectrum rather than just 4% that is absorbed by conventional UV-active materials as TiO$_2$ [3]. On the other hand these photocatalyst demands that their band-edges straddle the redox-potential of water, to enable it to be used as visible-active photocatalysts [4]. In order to identify or engineer such challenging photocatalysts, the knowledge of their electronic and optical structure is of immense utilization. We discuss here that how a correlation of theoretically computed electronic-structure and experimentally obtained physico-chemical properties can be a useful tool specifically in case of certain metal-oxide photocatalysts.

Unlike, UV-active photocatalyst, visible-active photocatalysts gained lot of attention during recent times [5, 6]. Iron containing oxide and tin containing metal oxides are known to occur naturally...
on earth. Thus, Ferrites viz. Fe₂O₃, MFe₂O₄ (M- metal ion) and stannate viz. SnO₂, BaSnO₃ have been investigated in view producing the eco-friendly visible light active photocatalysts. On the other hand, PbBi₂Nb₂O₉ type niobate system, one of efficient visible active material photocatalyst is also presented in the study. It is interesting to understand the effect of electronic structure on the photocatalytic or photoelectrochemical performance of the material. We show here the results of the theoretically computed properties, and experimentally observed properties of three different viz. ZnFe₂O₄ (ZFO), BaSnO₃: Pb (BSPO) and PbBi₂Nb₂O₉ (PBNO). The summarized results were further used to conclude the efficacy of visible light active photocatalyst for photo-splitting of water to generate the renewable energy.

2. Theoretical and Experimental Methods

2.1. Computational details

In order to simulate the electronic or optical structure of metal oxides following methodology was followed. Accordingly, theoretical calculations were performed with the full potential linearized augmented plane-wave (FP-LAPW) method as implemented in the Wien97 code with density functional theory (DFT) in generalized gradient approximation (GGA) [7]. In the LAPW method the unit cell is divided in two types of regions, one with the atomic spheres centred upon nuclear sites and other being the interstitial region between non-overlapping spheres. Inside the atomic spheres, the wave functions are replaced by linear combination of atom like wave functions, while in the intersphere region the wave functions are replaced by plane wave-like expansion. The muffin-tin radii for various atoms were chosen in the range of 2.0-1.6 a.u. in these calculations. The convergence parameter RK_max was set to 6.0. The calculation was iterated with the charge convergence criteria of 0.0001. Depending on the case the self-consistency was carried out on a 10/18 k-point mesh in the irreducible Brillouin zone for peticular system. In addition for a typical example of BaSnO₃: Pb, a fine mesh of 100 k points in the irreducible Brillouin Zone (BZ) of cubic unit cell was used to calculate the frequency dependent absorption coefficient I(ω) from real and imaginary parts of dielectric function ε(ω) = ε₁(ω)+iε₂(ω). A procedure similar to Gupta et al [8, 9] was adopted for these calculation of I(ω) which is given as $I(\omega) = \sqrt{2(\omega)} \left( \sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega) \right)^{1/2}$. The atomic coordinates were directly adopted from literature as reported earlier in our past work [9-11].

2.2. Preparation of photocatalysts

ZFO and BSPO

The powder photocatalysts of ZFO and BaSnO₃:Pb (BSPO) were prepared by chemical as well solid state reaction method as described below. The samples were synthesized by modified citrate complex method [12-14] in which typically stoichiometric concentration of Zinc nitrate hexahydrate (Zn(NO₃)₂): iron nitrate nona hydrate (Fe(NO₃)₃.9 H₂O) were mixed in 0.4 mol ethylene glycol (Mallinckrodt Chemicals AR grade) to which 0.1 mol of citric acid (Fischer Chemicals, 99.5 %) was added. Thus obtained mixture was stirred at 60 °C to obtain a thick brown (yellow) colored viscous solution, which was further heated for more than 10 hrs at 130 – 140 °C to finally obtain brown or dark brown color gel. The thick gelatinous liquid was further heated in alumina boat to 350 °C for 8 hr in an electric furnace. Thus resulting brownish black powder was crushed and calcined at various temperatures in the range of 600-1200 °C for 10 hrs. This yielded the desired spinel (cubic perovskite) metal oxides. BaPb₂Sn₁₋₃O₇ samples were prepared by following similar protocol. Accordingly, Barium nitrate, stannous chloride and lead acetate were used as respective precursor. The lead precursor concentration was varied from 0.1mol to 0.8 mol to increase the Pb doping concentration. Thus, this enabled us to obtain pale white, yellow, red, brown, black colored powders.
PBNO
In order to synthesize the powder photocatalyst of PBNO by solid state reaction method, a stoichiometric mixture of PbO, Bi2O3, and Nb2O5 was ground in a mortar and dried in an oven. Pelletized powders were calcined at 1273 K for 24 h in static air and sintered at 1200 °C for 24 h. Thus obtained powder was used for photocatalytic experiment. TiO2-xNx was prepared by the reported procedure [15]. The photocatalysts were loaded with 0.1 wt% Pt by impregnation with PtCl2, and further used for the photo-splitting experiments.

2.3. Characterization of photocatalyst systems
The photocatalysts were comprehensively characterized before being subjected to photochemical experiments. Structural phase confirmation being the first important objective, X-ray diffraction (XRD) studies was carried out for all photocatalysts. An advanced XRD equipment (Bruker AXS D8) that is equipped with a Lynx eye detector and CuKα(1.542Å) radiation was used to ascertain the sample phase compositions, within the detection limit of this technique. The accelerating potential and the filament current were fixed to 40kV and 40mA respectively. The XRD scan was recorded in the range of 20-80° 2θ angles with a step size of 0.01°. The results were compared with the respective standard JCPDS cards. The optical properties were studied by UV-Visible Diffuse reflectance spectroscopy (DRS) using Perkin-Elmer Lambda-750 spectrometer in the wavelength range of 200-800nm. The raw data obtained was further analyzed in detail. For the sake of normality other morphological studies were also carried out but not described here.

The photocatalytic behavior of the photocatalysts was studied by carrying out the photocatalytic hydrogen and oxygen evolution studies. Accordingly, the photocatalytic hydrogen/oxygen (over ZFO, PBNO/BSPO) evolution was studied under visible light irradiation (λ≥420nm). A typical schematic of photocatalytic experimental setup is shown in figure 1. As seen, the Hg-arc lamp (S) was connected to collimator and infra-red (IR) water filter to avoid heating of the reaction mixture. A cut-off filter was used to select the visible light (λ>420nm) for carrying out the reaction at the desirable wavelength. For hydrogen evolution studies known fixed weight of the photocatalyst was taken in a pyrex/quartz cell containing water-methanol mixture, the solution was purged with nitrogen prior to irradiation. The rate of H2 evolution was detected using a gas chromatograph (Shimadzu 2010AFT) equipped with a thermal conductivity detector. For hydrogen evolution study, typically light was made “ON” for certain duration of time evolved hydrogen gas was estimated. Under Light “OFF” there was no evolution of gas. Similarly, for oxygen evolution studies and aqueous AgNO3 solution was used during the experiments.

Figure 1. A typical schematic of experimental setup used to carryout the photocatalytic reactions and estimate the quantitative gas evolution.
3. Results and Discussions

3.1. ZnFe$_2$O$_4$ photocatalyst system

Structural characterization of the photocatalysts was carried out to study the calcination temperature dependent crystal phase evolution. Figure 2 displays the XRD pattern of the samples calcined at

![XRD spectra of different samples of ZnFe$_2$O$_4$ prepared by polymer complex methodology and calcined at various temperatures in the range of 500°-1200°C, for 4h.](image)

Figure 2. XRD spectra of different samples of ZnFe$_2$O$_4$ prepared by polymer complex methodology and calcined at various temperatures in the range of 500°-1200°C, for 4h.
various temperatures, showing the peaks related to the \( \text{ZnFe}_2\text{O}_4 \) crystal structure. The formation of the spinel \( \text{ZnFe}_2\text{O}_4 \) structure, along with the other impurity phases, was observed in all the samples calcined in the range of 500 - 700°C. The sample calcined in the range of 800 - 1200°C exhibited a single \( \text{ZnFe}_2\text{O}_4 \) phase without any impurity phase. This indicates that by making use of the chemical method, the \( \text{ZnFe}_2\text{O}_4 \) phase can be formed at a low temperature, yielding a pure phase at relatively lower temperatures [16, 17].

Figure 3 shows the UV-Vis diffuse reflectance spectra (DRS) for the ZFO sample calcined at 1000 °C and the \( \text{TiO}_{2-x}\text{N}_x \) sample, indicating that ZFO efficiently absorbs the visible light photons. The ZFO sample showed a sharp edge without a shoulder indicating that absorption can be attributed to an intrinsic band transition. It is known that, in spinel \( \text{ZnFe}_2\text{O}_4 \), the band structure is defined by the O2p valence band (VB) and the Fe3d conduction band (CB). Thus, the \( \text{ZnFe}_2\text{O}_4 \) absorption can be attributed to the photo-excited electron transition of O2p \( \rightarrow \) Fe3d [18]. On the contrary, \( \text{TiO}_{2-x}\text{N}_x \) showed two absorption edges; a main edge due to the oxide at 390 nm and a shoulder due to the nitride at 451 nm [15]. Estimated band-gaps were found to be 1.90 eV and 2.76 eV, respectively, for ZFO and \( \text{TiO}_{2-x}\text{N}_x \). The dark brown and yellow colors of these materials also indicate that they absorb visible light photons, as desired for a visible-light photocatalyst.

Figure 4 shows the computed total and the projected partial density of states (DOS) of \( \text{ZnFe}_2\text{O}_4 \) spinel lattice structure. The inset of the figure shows the schematic of spinel lattice used in the present computation studies. The DOS clearly reveals that Fe-d orbital contributes to the states in the inter-band forbidden gap of ZFO. The observation of DOS indicates that VB is constituted of dominant O2p
Figure 4. Calculated total and projected partial density of states (DOS) of spinel ZnFe$_2$O$_4$ crystal structures using FLAPW. The Fe-contribution to DOS is distinctly shown (red shaded area) revealing its importance in the formation of d-band in forbidden region. The unit of each vertical axis is states/(eV/unit). Fermi level is adjusted to 0eV. Inset shows the schematic of spinel unit cell.

rbital, whereas CB is composed of Zn-$d$ states, thus indicating the forbidden gap of ZFO. However, the dominant effect of $d$- orbitals is clearly revealed from the DOS studies. The Fe-PDOS shows a dominant contribution in the forbidden gap making ZFO suitable to absorb low energy photons. The calculated DOS shows a displaced valence band signifying it’s the $n$-type conductivity. However, in present case the Fermi-level is adjusted to 0eV as a general convention utilized during reporting the DOS studies. The Fe-PDOS shown by shaded area (red colour) indicates that they promote the inter-band transition in the band gap of ferrite systems, thereby making them absorb the low energy photons. This is in accordance with the observed optical absorption spectra of Fig. 3(a) that shows that ZFO strongly absorb in the range of 400-700nm wavelength range.

3.2. BaSnO$_3$: Pb photocatalyst system

Figure 5 shows the effect of Pb substitution on the XRD pattern of different BaPb$_x$Sn$_{1-x}$O$_3$ ($x \sim 0$ to 1) samples. The spectra reveal that as the Pb concentration increase from $x=0$ to 1, the 110 reflection of cubic BaSnO$_3$ structure shifts towards the lower 2$\theta$ values, finally yielding a structure close to the cubic BaPbO$_3$ in case of highest value of $x$. This clearly indicates that the degree of Pb incorporation in the BaSnO$_3$ cubic structure increases with the increase in Pb doping concentration. The existence of Pb as confirmed by energy dispersive spectroscopy (not shown here) is in line with the above fact. The
additional impurity peaks are due to the possible existence of trace amounts of BaO, SnO$_2$ or PbO phases. A detail analysis shows that there is concentration dependent increase in the lattice constant from BaSnO$_3$ ($a=4.1163$ Å) [19] to BaPbO$_3$ ($a=4.262$ Å) [20]. The increase in lattice constant ($a$) is expected due to the difference in the ionic radii of Sn$^{+4}$ (8.3 Å) and Pb$^{+4}$ (9.1 Å).

The photon absorption (UV-Vis) experiments are necessary to understand the optical response of

![XRD spectra of BaSnO$_3$:Pb with different Pb doping concentration](image)

**Figure 5.** XRD spectra of BaSnO$_3$:Pb with different Pb doping concentration, indicating the concentration dependent transformation from BaSnO$_3$ to BaPbO$_3$. The red dotted line indicates the concentration dependent change in 2θ, induced due to Pb-doping.
any material. The UV Visible DRS for the BSPO samples is displayed in Fig. 6. It can be noted that the absorption of BaSnO$_3$ clearly extended to the whole visible region (maximum to $\lambda>$750nm) with the increase in the Pb doping level. This is an important aspect desired for solar active materials. With the Pb doping level of $x=0.45$, the absorption significantly enhanced for the photons around wavelength of $\lambda>$450nm. For the higher Pb doping levels, the absorption totally extended to the visible region of electromagnetic spectrum, indicating that BSPO structures (for $x>0$) absorb the photons necessary for a visible light active photocatalyst. It was observed that for $0>x>1$ in BSPO, the white color of BaSnO$_3$ changes to yellow, reddish brown, dark brown and finally to black. This clearly demonstrates the tunability of the spectral response in the BSPO structures and thereby their potential usefulness in the visible light optical applications.

Figure 7 shows the computed total and the projected partial DOS BaPb$_{0.5}$Sn$_{0.5}$O$_3$, along with calculated absorption coefficient $I(\omega)$ of the BaPb$_{0.5}$Sn$_{0.5}$O$_3$ structure, as a function of photon energy. The comparison is made with the computed absorption of BaSnO$_3$ structure, indicating a clear increase in the visible photon absorption for BSPO (see magnified inset of Figure 7(b)). It is clearly evident from Pb-PDOS (Figure 7(a)) that Pb-6$s$ orbital controllably affects the bottom of CB of BaSnO$_3$. It further reveals that, in forbidden gap, the dominant contribution to the top of VB comes from the O 2$p$ orbitals, while the states at the CB minimum are predominantly due to Sn 5$s$ and Pb 6$s$ states. Thus, the Pb substitution induces the Pb 6$s$ states, which are located close to the lower edge of the CB to form a lowest unoccupied band. This kind of Pb doping renders the solar photo activity to photocatalytically inactive BaSnO$_3$. This is validated by the experimental confirmation as seen in Figure 6. Additionally, the doped system was found to photo-oxidize the water molecule under visible light irradiation as described in later section.
Figure 7.(a) Theoretically calculated total and partial DOS for BaSnO$_3$:Pb indicating the role of Pb-6s orbital (shaded in red) in the forbidden gap. The Fermi level is set at 0 eV. Inset shows the magnified view of DOS from -0.5 to +5 eV.
Figure 7(b). Computed absorption coefficient $I(\omega)$ of the BaSnO$_3$ and Pb doped structure as a function of photon energy. The inset clearly shows the enhanced absorption in doped sample.

3.3. PbBi$_2$Nb$_2$O$_9$ (PBNO) photocatalyst system

Figure 8 displays the results of structural and optical characterisation of most important photocatalytic system under study. The XRD pattern in Figure 8(a) exhibits the formation of highly crystalline PbBi$_2$Nb$_2$O$_9$ aurivillius perovskite phase [11] identified with a space group of $A21am$, $a = b = 5.496\,\text{Å}$, $c = 25.55\,\text{Å}$. It is known to posses a layered structure as shown in the right corner structure model. Figure 8(b) showing the UV-Visible diffuse reflectance spectrum over the range of 200 – 800nm is compared along with the spectrum of TiO$_{2-x}N_x$, indicating larger absorption by PBNO in the visible region of electromagnetic spectrum. It shows a conspicuous absorption edge indicating its low-band gap (2.88eV); in contrast, as mentioned earlier section, TiO$_{2-x}N_x$ displays an absorption alongwith a weak shoulder at around 451nm. This clearly indicates the superior optical property of PBNO system.
Figure 8. XRD (a) and UV-Vis DRS spectra (b) for PbBi$_2$Nb$_2$O$_9$. Inset in (a) shows the unit cell for the corresponding orthorhombic phase. TiO$_{2-x}N_x$ spectrum is used as reference.
Figure 9 shows the computed total and the projected partial DOS of PBNO lattice structure. According to the DFT calculation, we found that the band gap energy of PBNO was less than 2.88eV. The result illustrated in Figure 9 ascertains that in such compounds, the empty Nb4d and occupied O2p orbital are contributing to the formation of CB and VB, respectively. Importantly, the hybridization of the occupied Pb6s and O2p orbital seem to result in a narrower band gap in PBNO. This hybridization would push up the position of the valence band giving the smaller band gap compared to their respective lead-free counterparts. The Bi6s orbital is also located nearby and seems to form hybridization with O2p orbital (O2, O3 and O5 in Figure 9), although this hybridized band of Bi6s and O2p is located below the top of the valence band. The study clearly indicates that the Pb-6s orbital contributes to the top of VB in PBNO.

Figure 9. The computed total and the projected partial DOS of PBNO lattice structure indicating the role of different orbital towards the total DOS. Fermi energy was set to 0eV.
Table 1. Photocatalytic activities for respective H$_2$ evolution with sacrificial agent and O$_2$ evolution in presence of electron scavenger.

| Catalyst                 | Band Gap Energy (eV) | Hydrogen Evolution (μmol/gcat.hr) | Oxygen Evolution (μmol/gcat.hr) |
|--------------------------|----------------------|-----------------------------------|---------------------------------|
| $^{a}$ZnFe$_2$O$_4$      | 1.9                  | 1.3                               | NR                              |
| $^{b}$BaSnO$_3$:Pb       | VL                   | NF                                | 32                              |
| $^{a}$PbBi$_2$Nb$_2$O$_9$| 2.88                 | 7.6                               | 520                             |
| $^{a}$TiO$_2$:N$_x$      | 2.73                 | Trace                             | 221                             |

$^a$Catalyst loaded with 0.1wt% Pt, 0.3g; light source, 450W Hg-Arc lamp (Oriel) with UV cut-off filter ($\lambda \geq 420$nm). Reaction was performed in aqueous methanol solution (methanol 30ml + distilled water 170ml) for the half-reaction of water-splitting.

$^b$Photocatalytic oxidation was under $\lambda \geq 420$nm, was tested for 0.1g sample in presence of 0.01M AgNO$_3$ as electron scavenger with 300W Xe arc lamp (Oriel); VL-full visible range; NR-Not reported for this half reaction; NF-Not favourable band conduction band.

4. Photocatalytic perception: Band energetics for ferrites, stannates and niobates

![Figure 10](image)

Figure 10. The schematic band diagram for ferrite, stannate and niobate indicating the role of Fe/ Pb orbital towards photocatalytic behaviour.

As described in above section, we have systematically presented the experimental and computed results for respective important system of Ferrite, stannate and niobiate. Table – I shows the results of the photocatalytic experimentation on these systems. It shows the band gap energies, and respective hydrogen or oxygen evolution over the photocatalyst under consideration. These results are compared
with those of known visible light active reference photocatalyst of TiO$_2$-$\text{N}_x$. All are found to be photocatalytically active systems, for hydrogen or oxygen evolution. However, in each low band gap system, the role of orbital around VB and CB, are decisive in controlling the photocatalytic mechanism. This can be easily understood from the schematic given in Figure 10 as deduced from respective DOS studies. It clearly reveals the role of Fe and Pb orbital in ZFO and BSPO/PBNO respectively. It is noteworthy that Fe-$d$ orbital controllably induce the mid band gap states, such $d$-$d$ transitions enable the absorption of visible light photons, thus making it visible-active photocatalyst that can generate photocatalytic hydrogen. The role of Pb-$6$s orbital is interestingly different in case of BSPO and PBNO type systems. The Pb-$6$s orbital is found to contribute to the bottom of CB in case of BSPO; in contrast, it contributes to the top of VB in case of PBNO. In either cases, the role of Pb 6$s$ orbital is highly important. Accordingly, in case of BSPO, it converts photocatalytically inactive BaSnO$_3$ (>3.2eV) system into visible active photocatalyst. In case of PBNO type materials, it not only narrows the band gap of corresponding lead-free counterpart [11] of (Bi$_2$O$_2$$^{2+}$)(A$_m$B$_m$O$_{3m+1}$)$^{2-}$ [say here A=Pb, B=Nb; $m=2$] but also yields an efficient visible light active photocatalyst.

The above discussion demonstrates that the correlation of experimental observations with computed electronic structure is very useful in improvement of understanding of the photocatalyst materials. Such correlation is very desirable to discover new solar active materials for solar energy related power generation.

5. Acknowledgement

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6. References

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