Synthesis and Characterization of Sn$^{2+}$- based and Bi$^{3+}$- based metal oxides for photocatalytic applications

Dissertation by

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In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

King Abdullah University of Science and Technology

Thuwal, Kingdom of Saudi Arabia

July, 2016
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2016
ABSTRACT

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Dalal Aref Noureldine

The main challenge of water splitting technology is to develop stable, visible responsive photocatalysts that satisfy the thermodynamic requirements to achieve water redox reactions. This study investigates development of the semiconductors containing metals with $s^2d^{10}$ electronic configuration such as Sn$^{2+}$ or Bi$^{3+}$ which shifts the valence band position negatively. Efficient water splitting can, however, be only achieved by understanding the fundamental semiconductor properties of underlying processes. This work elucidates the semiconductor properties through two approaches: the first is to synthesize the materials of various stoichiometry in various forms (powders, thin film etc.) and the second is to perform a combined experimental-theoretical studies to determine the optoelectronic properties of the synthesized materials.

The study includes the synthesis and characterization of a series of Bi$^{3+}$ based semiconductors (Bi$_2$Ti$_2$O$_7$, Bi$_{12}$TiO$_{20}$, and Bi$_4$Ti$_3$O$_{12}$) to resolve inconsistencies in their optoelectronic properties. The crystal parameters and stoichiometry were confirmed by the Rietveld refinement and XRD measurements. These compounds showed a UV responsive absorption, high dielectric constants, and low electron and hole effective masses in one crystallographic reflecting their good charge separation and carrier diffusion properties. The approach showed to be accurate in determining the optoelectronic properties due to good agreement between experimental and theoretical values.
The second study investigated the synthesis of SnNb$_2$O$_6$ and using flux assisted method which afforded control over the surface. Increasing the flux to reactant molar ratio resulted in a 2D platelets with anisotropic growth along bc plane as confirmed by XRD and SEM. The photocatalytic activity increased while increasing the flux to reactant ratio exceeding solid state synthesis. This method minimized the oxidation of the surface and formation of grain boundaries and enabled the synthesis of the compound at lower temperature.

Next, the optoelectronic properties of $\alpha$-SnWO$_4$ structure were studied though a combination of experimental and theoretical approach. $\alpha$-SnWO$_4$ thin films were deposited by RF-sputtering. An interesting low band gap of $\sim$ 1.95 eV was experimentally for direct band gap and 1.7 eV for indirect band gap, high dielectric constants and low electron effective masses in one crystallographic direction were obtained, exhibiting good charge separation and charge carrier transport of the charge carriers. The PEC performance was limited by the oxidation of Sn$^{2+}$ in the material under applied potential.

Finally, pyrochlore SnSb$_2$O$_6$ structure was synthesized utilizing soft hydrothermal method. The crystal structure was studied by Rietveld refinement and the position of Sn$^{2+}$ was specified. The material showed interesting absorption edge around 700 which is promising for overall water splitting application.
ACKNOWLEDGMENTS

First and foremost, I want to thank my advisor Prof. Kazuhiro Takanabe for his continuous support throughout my Ph.D. Thank you for teaching me professionalism and hard work.

Committee members, Prof. Frank Osterloh, Prof. Omar F. Mohammed, Prof. Tao Wu, thank you for being my Ph.D dissertation committee members. Furthermore, I would like to thank Prof. Luigi Cavalo and his team for the collaboration of the theoretical calculations. Thanks to Dr. Moussab Harb and Ms. Sheikha Lardhi who performed the DFT calculations. Throughout my Ph.D learning journey, many postdocs and researchers have contributed to enrich my knowledge. Dr. Dilshad Masih, Dr. Manas Bhunia, Dr. Tarek Kandiel, Dr. Samy OuldChikh, and especially Dr. Ahmed Ziani. Thank you Dr. Ahmed for all your help and support not only scientifically but also personally. My colleagues in the group Ela, Angel, Amal, Nikos, Sean, Tatsuya, Muhammad and Anaam, thank you for adding fun to science.

Thanks to my amazing sisters Alaa, Zeinab and Jinan; you brought happiness to my heart, cheering me through my most gloomy days. To my amazing husband who always pushed me towards my ambitions, thank you for being extremely understanding for my busy life, the distance between us, and for all your love and support. To my queen, companion and my precious baby “Reine”. I could never be more thankful for your presence in my life, God’s greatest blessings. Finally, all my scientific efforts, dreams, ambitions would never exist without my super parents. My mother and Father, I would say an infinite thank you for all your sacrifices for me and my daughter. I owe my success for you

To my wonderful family
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<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AM 1.5G</td>
<td>air mass 1.5 global solar spectrum</td>
</tr>
<tr>
<td>AQE</td>
<td>apparent quantum efficiency</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller theory</td>
</tr>
<tr>
<td>CE</td>
<td>counter electrode</td>
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<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>EC</td>
<td>electrocatalyst</td>
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<tr>
<td>EDX</td>
<td>energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>HER</td>
<td>hydrogen evolution reaction</td>
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<tr>
<td>HOR</td>
<td>hydrogen oxidation reaction</td>
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<tr>
<td>HRTEM</td>
<td>high resolution transmission electron microscope</td>
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<td>IEA</td>
<td>International Energy Agency</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
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<tr>
<td>IR</td>
<td>infrared radiation</td>
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<tr>
<td>MW</td>
<td>molecular weight</td>
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<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
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<tr>
<td>OER</td>
<td>oxygen evolution reaction</td>
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<tr>
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<td>oxygen reduction reaction</td>
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<td>quantum yield</td>
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<td>RHE</td>
<td>reversible hydrogen electrode</td>
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<td>SBH</td>
<td>Schottky barrier height</td>
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<td>semiconductor</td>
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<td>SEM</td>
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<td>STEM</td>
<td>scanning transmission electron microscopy</td>
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<td>STF</td>
<td>solar-to-fuel</td>
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<td>solar-to-hydrogen</td>
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<td>solar to hydrogen conversion efficiency</td>
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<td>thermogravimetric analysis</td>
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<td>transmission electron microscopy</td>
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<td>UV</td>
<td>ultraviolet light</td>
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<td>visible light</td>
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<td>working electrode</td>
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<td>X-ray photoelectron spectroscopy</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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<td>$C$</td>
<td>F</td>
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<tr>
<td>$I$</td>
<td>A</td>
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\( i \) \( \text{A} \) current

\( j \) \( \text{A m}^{-2} \) current density variable

\( j_0 \) \( \text{A m}^{-2} \) exchange current density

\( \eta \) \( \text{V} \) overpotential

\( \eta_E \) energy efficiency

\( \eta_F \) Faradaic efficiency

\( \eta_{STH} \) solar-to-hydrogen conversion efficiency

\( a \) activity coefficient

\( z \) number of transferred electrons

\( B_T \) \( \text{V dec}^{-1} \) Tafel slope

\( n, p \) \( \text{m}^{-3} \) electron and hole concentration

\( n_i \) \( \text{m}^{-3} \) intrinsic carrier concentration

\( n_0, p_0 \) \( \text{m}^{-3} \) quasi-equilibrium carrier density

\( N_d, N_a \) \( \text{m}^{-3} \) donor and acceptor density

\( N_C, N_V \) \( \text{m}^{-3} \) effective density of states, conduction/valence band

\( J_n, J_p \) \( \text{A m}^{-2} \) electron and hole current density

\( U_n, U_p \) \( \text{m}^{-3} \text{s}^{-1} \) net electron and hole recombination rate

\( G_n, G_p \) \( \text{m}^{-3} \text{s}^{-1} \) electron and hole generation rate
$R_n, R_p$  \(m^3 s^{-1}\) electron and hole recombination rate

$D_n, D_p$  \(m^2 s^{-1}\) electron and hole diffusion constant

$\mu_n, \mu_p$  \(m^2 V^{-1} s^{-1}\) electron and hole mobility

$\tau_n, \tau_p$  \(s\) electron and hole lifetime

$\tau_c$  \(s\) collision time

$\sigma$  \(S m^{-1}\) electrical conductivity

$P_0$  \(m^2 s^{-1}\) photons absorbed from AM 1.5G

$P_{total}$  \(W m^{-2}\) incident power density in AM 1.5G

$x$  \(m\) depth into the bulk of a semiconductor

$x_s$  \(m\) radius of the particle

$\rho$  \(m^{-3}\) space charge density

$W_D$  \(m\) depletion layer width

$L_n, L_p$  \(m\) electron and hole diffusion length

$L_D$  \(m\) Debye length

$\chi$  \(eV\) semiconductor electron affinity

$\Phi_M$  \(eV\) metal work function

$E_g$  \(eV\) band gap

$E_{redox}$  \(eV\) standard redox potential
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<td>eV</td>
<td>semiconductor Fermi level</td>
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<td>$E_{fm}$</td>
<td>eV</td>
<td>metal Fermi level</td>
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<td>$E_{fn}, E_{fp}$</td>
<td>eV</td>
<td>quasi-Fermi level of electrons and holes</td>
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<td>$E_C$</td>
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<td>effective electron and hole mass</td>
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<td>$v_n, v_p$</td>
<td>m s$^{-1}$</td>
<td>recombination velocity</td>
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<tr>
<td>$A$</td>
<td>m$^2$</td>
<td>effective area</td>
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CHAPTER 1

Introduction

“Thirty years from now there will be a huge amount of oil – and no buyers. Oil will be left in the ground. The Stone Age came to an end, not because we had a lack of stones, and the oil age will come to an end not because we have a lack of oil.”

Former Saudi minister of Oil, 2000

Sheik Ahmed Zaki Yamani

1.1. Hydrogen gas as future fuel

Energy is one of the most crucial topics for the development of human civilization. It has become as essential as food and water to human’s life. Since the Industrial Revolution in the 19th century, the world has experienced an exponential increase in the demand for energy. This dramatic rise in demand is associated with advances in technology, which have created an irreversible change in the lifestyle that human beings witnessed as a society. Therefore, to keep up with society demands, energy is necessary to ensure a continued high standard of living.

However, the current energy system is heavily reliant on fossil fuels, mostly in the forms of oil, coal, and natural gas. The fossil fuels contribute to almost more than 87% of primary power supply. Continued reliance of these fuels presents 3 main disadvantages: 1) they are
limited and non-renewable energy sources; 2) formation of carbon emissions by combustion; and 3) their geographically localized nature.

The current reserves of fossil fuels were generated through through different biological and inorganic systems over the course of millions of years.\textsuperscript{1,2} On the other hand, the current energy consumption rate grew at an average rate of 3\% per year between 2002 and 2012.\textsuperscript{6} Based on this rate, fossil fuel reserves will fall in shortage as estimated by 2088.\textsuperscript{3}

Furthermore, even if fossil fuels were everlasting sources, the created air pollution threatens the human existence. The combustion of fossil fuels results in generation of greenhouse gases; in particular carbon dioxide (CO\textsubscript{2}), nitric oxide (NO\textsubscript{x}), and methane.\textsuperscript{4} Carbon dioxide emissions have increased by 90\% since 1970 with 70\% of these emissions arising from fossil fuel combustion.\textsuperscript{5} This is concerning because increased greenhouses gases in atmosphere will result in more trapping of sunlight by the earth and this will in turn increases the earth’s temperature. This phenomena which is known as global warming has severe consequences such as melting of polar ice, rise in the sea levels, flooding, and destruction of food crops. Here comes the implication of the quote of Sheik Ahmed Zaki Yamani, cited above; humans must find alternative future fuels to ensure the continued survival of human civilization.

Any future fuel must exhibit several characteristics to overcome the limitations of fossil fuels. First, it should be clean with no carbon emissions. Furthermore its storage, handling, and distribution must be done in an environmentally benign ways.
Second, the future fuel must respond to the increasing energy demands, hence it must ensure a constant and stable energy flux. This indicates that its production may come from sustainable sources and should not affected by factors such as weather and day/night shift.

Thirdly, the future fuel must be cost effective to be able to compete with current fossil fuel economy. Therefore, the technology adopted must be simple with minimum need to infrastructure.

Hydrogen gas meets the above criteria. It is a clean and high density energy carrier with an energy yield of 122 kJ.g\textsuperscript{-1} which is almost triple that of gasoline (40 kJ.g\textsuperscript{-1}).\textsuperscript{6} It has zero carbon emissions of greenhouse gases as it produces only water (ideally). Finally, having the energy stored in chemical bonds, this makes it transportable form of fuel which is critical to ensure the constant supply. It can be stored as a gas or liquid or in the form of metal hydride.

Hydrogen has attracted the scientific attention as the “future fuel” and research has been focused to generate hydrogen from a variety of sources. It can come from renewable energy such as wind, hydropower, geothermal and solar energy, from nuclear energy, or from cracking and steam reforming of fossil fuels. Figure 1.1 shows a summary of the possible pathways for hydrogen production.
Currently, the most utilized method to produce hydrogen is “steam reforming” process. This process utilizes methane as a feedstock due to its high hydrogen to carbon ratio, and it involves two main steps. Firstly, methane is mixed with steam and passed over a high temperature and high pressure bed resulting in the generation of Carbon monoxide (CO) and three hydrogen (H₂) molecules. The CO undergoes a shift reaction in the next step while reacting with excess steam producing CO₂ and H₂ gases. Therefore, this process is not cost carbon neutral and cannot produce hydrogen that would be considered a clean future fuel. Other methods of producing hydrogen from carbon sources suffer from the same problems, coal gasification.

Therefore, to meet the definition of a clean future fuel, hydrogen must come from renewable sources. One major challenge for some renewable sources is that although they are and unlimited, they cannot be stored directly. As shown in Figure 1.1 Starting from
wind, hydropower, geothermal or solar PV, is first used to produce electricity, then generated electricity will be used for electrolysis and hydrogen production.

For hydropower, the energy is produced starting from water through mechanical rotation of the turbines of a hydroelectric dam.\textsuperscript{10} the annual growth rate of this technology is still limited compared to other renewable technologies with 2\% annual increase.\textsuperscript{9} this limitation is due to the high cost of building the dams, and the ecological as well as geological damage associated with their construction.

Geothermal energy derived from heat extracted from deep underground water or rocks.\textsuperscript{11} this source of energy characterized by its rapid rate of extraction from the sources which makes it reliable source of energy. However, it suffers from limited lifetime and therefore requires continuous searching for new sources. This creates an additional cost on the electricity coming from these sources resulting in slow annual increase of 3\%.

The Solar photovoltaic field is the most advanced industry among the renewable energies. It has witnessed enormous growth at an average annual rate of 46.6\% since 1999.\textsuperscript{10} In the United States (US), an unprecedented 7.3 gigawatts of capacity were installed in 2015 and and total installed capacity is expected to increase by 119\% by the end of 2016.\textsuperscript{16} Despite the maturity of this technology, it is not the ultimate solution due to the limitations to high cost of electricity transport. Furthermore, the scalability of this technology demands covering large areas which requires high capital cost for installation and maintenance.\textsuperscript{17}

Therefore, it is clear that renewable sources that directly produce hydrogen are more favorable in terms of simplicity and cost. As seen in Figure 1.1, hydrogen is directly produced from either biomass or solar energy through direct solar water splitting.
The production of hydrogen from biomass can be attained through either thermochemical or biological processes. In both cases they require high temperature and pressure.\textsuperscript{12,13} However, the products are not carbon neutral as CO, CO\textsubscript{2}, carbon, and other carbon compounds are released as by-products.

Hence, direct solar water splitting is the most promising way to produce completely clean and renewable hydrogen gas as it utilizes the sunlight and water as raw materials which are both abundant, sustainable, and renewable. Approximately, $3.85 \times 10^{24}$ J of solar energy strikes the earth per year which is 4 orders of magnitude greater than the world’s energy consumption.\textsuperscript{14,15} Therefore, only 0.01% of the total solar energy needs to be efficiently used. Solar technologies must be innovatively developed to meet energy demand, in particular, large-scale, and simple technologies that can compete with current fossil fuels. So far, the water splitting using photocatalysts is still in its early stages of development, but holds great hopes within. The details of this technology will be discussed in the next section.

**1.2. Solar water splitting**

Nature perfectly stores chemical energy using sunlight through a complex process so-called “photosynthesis”.\textsuperscript{16} The biological components of the plants perfectly perform the absorption of sunlight using chlorophyll and the subsequent charge and proton transfer steps. Two reactions occur: 1) water splitting to produce oxygen, 2) Carbon dioxide fixation to produce the sugars.\textsuperscript{17}
Learning from nature can lead new era of “Artificial photosynthesis”. Indeed, it is not practical for humans to mimic the biological machinery of plants that have been developed through millions of years as it is expensive and would require significant time. Therefore, humans can still mimic photosynthesis, but using a photocatalyst to split water into its main components using sunlight which will be the ideal solution for energy problem. The water splitting reaction is attractive from economical point of view. This is due to the usage of abundant and free energy sources. In this process, the only reactant is water which will be decomposed utilizing sunlight into its main components hydrogen and oxygen which will be later separated. The approach is simple in which no additional electronic devices are required making it appealing in terms of large scalability and low capital cost minimizing the need for expensive infrastructure. The reaction is simple described by equation 1.1:

$$\text{H}_2\text{O} \rightarrow \text{H}_2(\text{g, 1 atm}) + \frac{1}{2}\text{O}_2(\text{g, 1 atm})$$

(1.1)

This reaction is two electron endothermic, with Gibbs free energy ($\Delta G$) = 237 kJ.mol$^{-1}$, hence additional energy is needed. The photon energy is generally described by the equation 1.2:

$$E = h\nu = \frac{hc}{\lambda}$$

(1.2)

Therefore for photons with energy of 1.23 eV are needed to drive the overall water splitting reaction. By simple calculation, this corresponds to wavelengths around 1000 nm. Since the reaction is uphill, a catalyst is needed to minimize the activation energy barrier of the reaction by providing alternative reaction pathway with lower energy barrier. By the
definition of the international union of pure and applied chemistry (IUPAC), \(^\text{22}\) “photocatalysis is a change in the rate of a chemical reaction or its initiation under the action of sunlight (ultraviolet, visible or infrared radiation) in the presence of a substance—the photocatalyst—that absorbs light and is involved in the chemical transformation of the reaction partners.

Hence, the photocatalyst should be a semiconductor with a band gap of at least 1.23 eV to absorb the photons. This is a thermodynamic requirement to provide the enough photo voltage to drive the overall reaction. Taking into account the over potentials needed to drive the Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) due to semiconductor-liquid interfaces (which will be described in detailed in section 1.3.), entropic losses and other heat losses, a band gap around 1.6-2.2 eV is considered ideal.\(^\text{23-27}\)

Another important thermodynamic requirement dictated is that the band edge positions should straddle the electrochemical potentials for OER and HER. That is the valence band should be more positive than the water oxidation potential and the conduction band should be more negative than the hydrogen evolution potential (0.0 V vs. RHE).

In addition, the semiconductor photocatalyst should exhibit stability in aqueous environment to be effective for long term operation. Finally, the cost and the abundance of the constituent elements are important to ensure that water splitting is possible on a large scale.\(^\text{37}\) Many inorganic semiconductors have already been reported to successfully split water, however none of them match all of these criteria.\(^\text{29}\)
So far, many configurations of photoelectrochemical (PEC) and photocatalytic water splitting have been studied. In the following section these technologies are described.

### 1.2.1. Technologies

The reaction of water splitting has been employed in different photocatalytic configurations. In order to be able to compare efficiencies of different systems two important efficiency terms are standardized.

The first is the solar to hydrogen which is defined by equation 1.3:

$$STH = \left[ \frac{J_{sc} \left( mA.cm^{-2} \times 1.23V \right)}{P_{total} \left( mW.cm^{-2} \right)} \right]_{AM 1.5G}$$  \hspace{1cm} (1.3)

Where the product of the current density ($J_{sc}$) and the voltage (1.23 V) is utilized to measure the chemical output power to the PEC water splitting cell, and the $P_{total}$ is the total input power under 1 sun AM 1.5 G illumination assuming 100% faradaic efficiency for conversion of water into $H_2$ or $O_2$.\textsuperscript{29}

It is important to note that the STH definition is correctly applied only for systems where water and sunlight are the only starting inputs and hydrogen and oxygen gases are the exclusive output.\textsuperscript{30}

In case of systems that do not comply with the definition of Solar to Hydrogen (STH) efficiency, another term is defined which is the external quantum yield (EQY) defined by equation (1.4). These systems utilize sacrificial reagents and perform only either the HER
or the OER half reactions =

\[ EQY = \frac{\text{# of product molecules} \times n}{\text{# of incident photons}} \]  

(1.4)

Where the variable “n” is the number of electrons transferred per product molecule.

The studied photocatalytic systems can be categorized generally into two main groups: the first involves photo electrochemical (PEC) panels in which the semiconductor is applied as an electrode, and the second in which the particulate photocatalytic (PC) are used for the water splitting system.

The PEC panels can be categorized into 3 categories:

1) The pure PEC which are made up of minority carrier devices processing single or dual PEC junction.

2) Single PEC junction panels coupled with integrated or external photovoltaic (PV) device.

3) PV device coupled with electrolyzer in an integrated structure which is immersed in water.

The particulate photocatalytic water splitting system has been deeply investigated in research and the developed configuration can be classified into three groups:

1) Single particle-single photon water splitting system: this type of configuration is capable of driving both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) using the same semiconductor without the need for an external redox couple. This is a true water splitting system that yields
stoichiometric amounts of hydrogen and oxygen gases. The highest external quantum yield (EQY) are attained by using semiconductors with large band gap ($E_g$). An EQY > 50% was obtained by a semiconductor system with and $E_g$ of 4.1 eV.\textsuperscript{31} This limits the beneficial utilization of visible sunlight. Domen and coworkers successfully performed true overall water splitting with an efficiency of 2.5 % at 420 nm using Rh\textsubscript{2-y}Cr\textsubscript{y}O\textsubscript{3} loaded (Ga\textsubscript{1-x}Zn\textsubscript{x})(N\textsubscript{1-x}O\textsubscript{x}).\textsuperscript{31}

2) The second category comprises the systems that involve two-particle-two photon water splitting. This is also referred to as a “Z-Scheme”. It also involves stoichiometric overall water splitting, but utilizes an intermediate redox couple between two separate photo absorber semiconductors. Each semiconductor is chosen to drive either the HER or the OER. This system has two main advantages; the first is that it provides higher voltage than single absorber system. The second, it enables larger range of semiconductor materials to be incorporated surpassing the thermodynamic requirement of straddling both hydrogen and oxygen evolution potentials.\textsuperscript{33, 34}

3) Although the third configuration is extensively studied in literature, it is not considered true water splitting system. It involves either the HER or the OER while the counter reaction is chosen to minimize the $\Delta G$ needed to drive the reaction.\textsuperscript{35} These systems can be applied in environmental fields such as decomposition of organic pollutants.\textsuperscript{36}

In designing the systems for overall water splitting, the cost-efficiency paradigm is crucial. The US Department of Energy (DOE) has set a target cost between $2.00-$4.00 for 1 Kg of H\textsubscript{2}. This price is comparable to the price of untaxed one gasoline gallon at the pump.
This is to ensure that the technologies adopted will be able to compete with the current fuel system. So far, four types of reactor design has been studied for the techno-economic analysis by DOE for centralized plant design. The reactor types are named Type I, II, III, and IV and are shown in Figure 1.2 below.

Figure 1.2. (a) Type I. Single electrolyte reactor-bed suspension (b) Type II. Dual electrolyte reactor-beds with photocatalytic colloidal suspensions that are independently catalyzing half-reactions with a membrane for gas separation and ionic transfer (redox mediator required). (c) Type III Monolithic PEC-panel based on multi-junction PV arrays. (d) Type IV Solar concentrator PEC water splitting reactor. Sensitivity analysis of the H$_2$ cost (right). The variability of the calculations based on the effects of the systems efficiency, particles or PV panels costs, and systems lifetime for the different reactor types.
These reactor models represent different examples of complete, simple and potentially applicable systems. Each of these systems contains all different components for photon absorption, generating the appropriate voltage to produce both O₂ and H₂ from water. The collection and the compression of the obtained gases is considered as well.

In general, type I and type II belong to particulate photocatalysts and types III and IV belong to the panels systems. The first two types are similar in their mechanism for overall water splitting. A single semiconductor material is utilized as the photocatalyst for type I generating both hydrogen and oxygen simultaneously in one compartment. This system is advantageous in terms of simplicity. The main difference between type I and II reactor is the use of separate beds utilizing an ionic bridge for redox couple. This provides two main advantages over system I. The first advantage is that two gases are readily separated. This enhances the safety of the system and minimizes the need for gas separation techniques and infrastructure. The other advantage is that this system opens the door for wider variety of semiconductors to be utilized. The type II system resembles the Z scheme described earlier.

In terms of design, the type I reactor system is simple composed of horizontal plastic bags (so-called baggie) containing the slurry of the photocatalyst (40 nm diameter). All the components are designed to be retained inside the baggie while the sunlight penetrates. As for type II, the continuous slurry of photoactive material circulates within the two baggies through a perforated membrane.
Reactor types III (fixed panel array) and IV (tracking concentrator array) are similar in their design. Both are made up of multilayer absorber planar arrays comprised between two electrodes and immersed into the aqueous solution. As shown in Figure 3 (c and d), both reactor types III and IV resemble commercial photovoltaic solar cells in their design. The main difference is the need for additional tracking concentrator that maximizes the capturing of the radiation. Therefore, system IV enables the usage of high efficiency but high cost material because the semiconductor material used in the photo reactor system is reduced.

In terms of cost, Figure 1.2. shows a detailed analysis of the cost break down of the four reactor systems. The effect of efficiency, particle or panel cost, and component lifetime on the cost of hydrogen from each reactor system is studied. In terms of cost, the cost of hydrogen is expressed in dollars per kg for each system, it represents the cost at the pump without and transportation. The four types of reactor showed prices of $1.6, $2.5, $10.4, and $4 for reactor types I, II, III, and IV respectively. It is worth mentioning that the levelized prices of type I and type II reactor still meet the DOE requirements even with a more conservative STH efficiency of 5% predicting hydrogen costs of $2.3 and $3.2 respectively. Eventually, It is valid to highlight that based on 3 techno economic studies, the particulate photocatalysis based systems prove to be more promising in terms of cost and technological feasibility.

Research interest needs to be oriented towards particle photocatalysts. It becomes indispensable to develop the suitable photocatalysts and improve their efficiency.
1.2.2. Mechanism of overall water splitting and Requirements of the bulk properties for an efficient photocatalyst

Particle photocatalysis systems have proven to be technologically attractive due to their simplicity as discussed earlier. Yet, the underlying mechanism for overall water splitting using a solid semiconductor is complex. And many physical processes are involved.

Figure 1.3 shows the scheme for overall water splitting reaction over solid semiconductor.

Figure 1.3 Scheme of the photon induced process for overall water splitting by solid photocatalyst.

The reaction is started by the process of light absorption. Upon illumination, the semiconductor absorbs photons with energy equal or greater than the band gap. Upon absorption, an exciton -electron-hole pair- is formed. The electrons are excited from the valence band into the conduction band leaving holes in the valence band and creating electrons in the conduction band. Taking into account the time scale of the process, the
absorption occurs in the femtosecond level. At a similar time scale, electrons in the conduction band and holes in the valence band will relax to the bottom of the conduction band and top of the valence band, respectively.\textsuperscript{40} The photo generated carriers will have to be successfully separated and transferred to the surface of the semiconductor photocatalyst. Once at the surface of the semiconductor, depending on the semiconductor-electrolyte or semiconductor-metal interfaces, the electrochemical reactions occur. The water reduction and oxidation reactions will occur in a time scale longer than microsecond.\textsuperscript{41}

In general, most of the photocatalysts reported so far has shown to be inactive to catalyze HER or OER. This is related to the over potentials at the surface. Hence, to accelerate the rates of these two reactions, cocatalysts which are mainly metal nanoparticles or metal oxides are added on the surface of the photocatalyst. They act as active sites for HER and OER minimizing the over potential needed by electrons and holes to drive these reactions. Another important advantage of the cocatalysts, is that they enhance the charge separation by finding a driving force of charge carriers to move to the surface and minimize the recombination between electron and holes.

To develop the ideal photocatalyst, the competing photo physical and chemical processes must be understood and optimized to enhance the efficiency of the reaction.

The processes that occur in the bulk are: light absorption, exciton separation, and carrier diffusion. And those that occur on the surface are carrier transport, catalytic efficiency, and mass transfer of the reactants. These fundamental physical processes occur sequentially. Figure 1.4. shows a scheme of each step and the key parameters that affect each step.\textsuperscript{15} These processes will be discussed in detail.
Figure 1.4. Summary of the fundamental photo physical and photochemical processes involved in the overall water splitting reaction. Each step is represented with a step with the controlling parameters. Inspired from K. Takanabe.¹⁵

Photon absorption
The bulk of the semiconductor is very important. By analogy to a real life ladder, if any step is missed the goal could never be achieved. Similarly, if any process in the bulk was not efficient enough, the electron hole pair will recombine and the reaction’s overall efficiency is limited.

The first step is light absorption in which the electron-hole pair are generated consequently. To attain maximum efficiency from this step, analysis of the solar spectrum is required.
Figure 1.5. shows the STH efficiency as a function of the wavelength based on data from solar spectrum of AM 1.5 G.\textsuperscript{42}

Detailed analysis of the solar spectrum is described elsewhere.\textsuperscript{15} In a brief summary, the largest energy portion of the solar spectrum is found in the visible region \((400 \text{ nm} < \lambda < 800 \text{ nm})\) which forms more than 54.1\% of the total energy. In comparison, only 9.3\% of the energy of the sunlight is found in the UV region.

Integrating the solar irradiance from UV to infrared around 1000 nm while assuming 100\% QE results in a maximum theoretical STH of 48\% approximately. In the UV region, the maximum theoretical STH is only 3.3\% which falls below the previously calculated benchmark STH efficiency of 10\%. Hence, the excess photons with energy greater than the band gap will be lost in form of heat or other forms of photo emissions.
Figure 1.5. Relationship between STH and photon wavelengths available at different AQYs for photocatalytic water splitting. It is assumed that two water molecules are split into two hydrogen molecules and one oxygen molecule in four-photon processes.\textsuperscript{45}

Therefore, the absorption must be shifted into the visible region in the wavelength range to meet technological requirements.

The absorption of the photons by the powder semiconductor involves intrinsic and extrinsic absorptions as well as scattering, reflection, and transmission processes.

Two types of scattering are generally known for the powder system: Rayleigh and Mei scattering. The former occurs in the particles with small scatter diameters while the latter occurs in larger ones.\textsuperscript{43} In addition to that, powders experience the processes of light reflection and transmission which are generally described by the Frenkel equations.\textsuperscript{44}

Here it is worth mentioning that the effect of reflection and transmission processes are completely different between a photoreactor containing the powder suspension in comparison with the film.

It is beneficial for the powder suspension since the scattered and reflected light are not lost but instead absorbed by other particles. This is not the case for the film in which scattering and reflection are lost which is detrimental in the case of the film. On the other hand, the thin film enables the measurement of the absorption properties of the semiconductor material which is not the case of the powder. In case of powder, the obtained spectra contain information about the band gap excitation, but also other phenomena such as d-d transition and addition phonon absorption or defect-state absorption.\textsuperscript{46} Therefore, it is hard to
accurately determine the absorption coefficient from the powders. The diffuse reflectance model is generally used to describe the absorption properties.\textsuperscript{44}

The Kubelka Munk function $f(R)$ is used to describe the absorption coefficient, reflectance and scattering:

$$f(R) = \frac{(1 - R)^2}{2R} = \frac{\alpha}{s}$$ (1.5)

Where $R$ is the reflectance, $\alpha$ is the absorption coefficient, and $s$ is the scattering coefficient. The $s$ value is often ambiguous and undetermined which makes it hard to extract the absorption coefficient and a film with known thickness becomes necessary to determine $\alpha$.\textsuperscript{47} Note that if the scattering coefficient is independent of $\lambda$, $f(R)$ is then proportional to $\alpha$. The band gap is still valid to be determined from the powder as it will discuss later in the section.

As mentioned earlier, the absorption coefficient ideally defines the absorption properties.

It is defined by equation below:

$$\alpha (cm^{-1}) = \frac{\ln(10) \times A}{l(cm)}$$ (1.6)

Where $l$ is the path length of the light through the sample.

In case of films the transmittance and reflectance can be measured and related to $\alpha$ by the following equations:\textsuperscript{47}

$$T = \frac{(1 - R')^2 e^{-\alpha d}}{1 - R'^2 e^{-2\alpha d}}$$ (1.7)
\[ R = R' \left( 1 + \frac{(1-R')^2 e^{-2ad}}{1-R'^2 e^{-2ad}} \right) \] (1.8)

Where \( T \) is transmittance, \( R \) is reflectance, \( R' \) is the single surface reflectance of the material and \( d \) is the distance. From these two equations the absorption coefficient can be defined in terms of \( T \) and \( R \) as:

\[
\alpha = -\frac{1}{d} \log \left( \frac{1+R^2 - 2R^2 - T^2 + \sqrt{(1+R^2 - 2R^2 - T^2)^2 + 4T^2}}{2T} \right) \] (1.9)

When \( R \) is negligible and/or when the following inequality is satisfied 48:

\[ Re^{-ad} \approx 1 \] (1.10)

Then the equation 1.9 can be simplified to

\[ T = (1-R)^2 e^{-ad} \] (1.11)

Which can be further rearranged and the absorption coefficient expressed by:

\[
\alpha = -\frac{1}{d} \ln \frac{T}{(1-R)^2} \] (1.12)

Another method to calculate the absorption coefficient is by analyzing the interference fringes in ranges where absorption is minimal.\(^{49}\) That being said, the absorption coefficient is a very important parameter which is utilized to define the penetration depth. The penetration depth is defined as the reciprocal of the absorption coefficient on the natural logarithmic scale.
It represents the distance to which the light can travel where intensity is decreased by 1/e around 36% of the initial intensity. This information is crucial for the design of the photo reactor, it allows to determine the number of the photocatalyst particles needed to absorb the incident light effectively.

Another important parameter is the nature of band gap. Currently, the electronic structure of the semiconductors can be accurately calculated through density functional theory (DFT) calculations. Briefly describing the concept of energy band, the electronic band structure is determined in solid state physics by the ranges of energy in which the electron is forbidden or allowed.

At infinite separation, the atoms are treated independently with atomic energy levels. When the atoms are brought close to each other in a molecular solid, multiple molecular bonds are created from the atomic orbitals. The atomic orbitals will split to accommodate all the electrons. The electrons are filled according to the Pauli’s exclusion principle.\textsuperscript{50,51,57} Consequently, the energy bands will be formed when large number of atoms are brought into contact which is the case of the solid crystal. The energy bands are composed of an enormous number of closely packed individual energy levels having finite energy widths. These bands are generally analyzed using quantum mechanics resulting into the energy diagrams.

Taking the periodic nature of the crystal structure into account, the electron’s wave function is defined by the Bloch theorem.

By rewriting the eign states (Ψ) the Bloch theorem results into a wave vector (k) which can be often confined to the first Brillouin zone. Detailed description is found elsewhere.[53]
Eventually as a result of solving the eigenvalue problem, the energy levels of an electron in a periodic potential are described in terms of a family of continuous functions $E_n(k)$:

$$H_k u_k = E_n(k) u_k(r)$$

(1.13)

Plotting $E$ vs. $k$ along with the high symmetry crystallographic direction in the crystal results into the dispersion or the band structure of a solid. This complex energy diagram can be further simplified into completely filled states (the valence band) and completely empty states (the conduction band).

Electronic band structure calculations have become increasingly important to understand the optoelectronic properties of the material. One important property related to absorption as mentioned earlier is the nature of the optical transition of the band gap. Two types of band gaps are generally defined: the direct band gap and indirect band gap.

For a direct band gap, the crystal orbitals at the highest point of the valence band and those on the lowest point of the conduction band lie along the same wave vector.

However, for an indirect band gap additional change in the crystal momentum is needed. This is because the maximum of the valence band and the minimum of the conduction band lie on different $k$ points which requires phonon and phonon absorption.

This main discrepancy in the nature of the band gap results in two different absorption coefficients. Semiconductors with direct band gaps are favorable due to their higher absorption coefficient compared to those with indirect band gaps.\textsuperscript{52}
Knowing the absorption coefficient in case of film and Kubelka-Munk in case of powders, the band gap can be calculated using the Tauc plot according to the following relationship: \[ \alpha h \left( h - E_g \right)^\frac{1}{n} \] (1.14)

Where \( n \) can take values of 3, 2, 3/2, or 1/2, corresponding to indirect (forbidden), direct (allowed), direct (forbidden), and direct (allowed) transition, respectively.\(^{46}\) Using the Tauc plot i.e. \( (\alpha h \nu)^\frac{1}{n} \) as a function of \( h\nu \) (\( n \) as defined earlier) the intersection of a line tangent to the slope in the linear region of the absorption onset with the baseline determines the band gap.\(^{46}\)

Understanding the parameters involved in the photon absorption step helps to optimize this crucial process. With the help of DFT calculations, the impractical screening process for suitable semiconductors can be avoided. Instead, information about the band gap and its nature, the band positions (vs. vacuum), the hybridization of the orbitals within the crystal structure, and absorption coefficient can be deduced by plotting the density of states which is the number of electronic states per unit energy interval.

Exciton separation

Following light absorption, the next step involves exciton generation.\(^{55}\) The exciton is defined as an excited electron-hole pair attracted with a binding energy. The exciton binding energy is defined as the energy needed to ionize an exciton in its lowest energy state.\(^{56}\) The exciton energy must be overcome for these charges to be separated into free
charge carriers and therefore used for the photocatalytic processes. Hence, low binding energy is generally required.

The Mott-Wannier exciton model is used for semiconductors which are characterized by high dielectric constant, low absorption coefficient and high exciton binding energy. Using this model, the energy of the 1s state an exciton can be described by:

\[
R_n = \frac{m^* e^4}{2\hbar^2 \varepsilon_r^2} = E_1 \frac{m^*}{\varepsilon_r^2}
\]

(1.15)

Where \(m^*\) is the reduced effective mass of the electron-hole system \(\left(\frac{1}{m^*} = \frac{1}{m_n^*} + \frac{1}{m_p^*}\right)\), \(\hbar\) is the Plank’s constant, \(e\) is the elementary charge and \(\varepsilon_r\) is the dielectric constant. The dielectric constant is defined as the charge retention capacity is a medium. The dielectric constant \((\varepsilon_r)\) is a frequency-dependent parameter and consists of two components:

1) Ionic vibrational polarization component \((\varepsilon_{\text{vib}})\) in strongly ionic compounds with soft vibrational modes

2) Electronic polarization component \((\varepsilon_{\infty})\). At high frequencies relevant to the UV-Vis region considered in photocatalysis \((10^{14}-10^{15} \text{ Hz})\) which can be found in high polarizability elements.

The dielectric constant is described by the complex index of refraction:

\[
N = n + ik
\]

(1.16)

Where \(n\) is the refractive index and \(k\) is the extinction coefficient. The refractive that can be determined from reflectance and transmittance spectra by the following equation:
\[ n = \frac{f(\lambda_1, \lambda_2)}{2(\lambda_1 - \lambda_2)t} \]  

(1.17)

Where \( f \) is the fringe number, \( \lambda_1 \) and \( \lambda_2 \) are the maximum and minimum wavelengths of the wave fringe and \( t \) is the film thickness. Knowing the absorption coefficient, \( k \) can be deduced by:

\[ k = \frac{\alpha \lambda}{4\pi} \]  

(1.18)

The complex dielectric constant is represented by:

\[ \varepsilon = \varepsilon_1 + i\varepsilon_2 \]  

(1.19)

Correlating the complex index to the dielectric properties, then the real part is \( \varepsilon_1 (\varepsilon_1 = n^2 - k^2) \), and the imaginary part \( (\varepsilon_2 = 2nk) \).

Therefore, in order to obtain low exciton binding energy, high dielectric constants are needed. In general, it was suggested by previous theoretical work that an exciton binding energy equal or less than 25 meV is suitable for charge separation at room temperature.\(^{58}\)

Not only the value of the exciton binding energy, but also its anisotropic nature is important. This requires a dielectric constant of at least a value of 10.

Currently, the DFT calculations have shown to be increasingly helpful to accurately predict the exciton binding energy and dielectric constant along different crystallographic directions. This is important where experimental measurements are hard to perform especially for the vibrational contribution of the dielectric constant.
Transport properties: Charge diffusion

Following the exciton separation, the free charge carriers must successfully transfer from the bulk of the semiconductor towards the surface and hence drive the photocatalytic reactions. This step is crucial for photocatalytic activity, and it is greatly affected by the mobility of the charge carriers, i.e. their ability to transport charges within the semiconductor material. Therefore, the factors that determine the transport properties are the diffusion coefficient, carrier mobility, and the life time of the charge carrier which are related through Einstein’s equations.

\[ D = \frac{k_B T}{e} \mu \quad (1.20) \quad \text{and} \quad \mu = e \frac{\tau}{m} \quad (1.21) \]

Where \( D \) is the diffusion coefficient, \( k_B \) is the Boltzmann constant, \( e \) is the elemental charge and \( m^* \) is the effective mass and \( \tau \) is the charge carrier life time.

The life time of the minority charge carrier is measured by spectroscopic techniques.[49]

It is expressed by the following general equation for quasi-steady state and quasi transient carrier life time measurements:

\[ \tau_{eff} = \frac{\Delta n(t)}{G(t) - \frac{d\Delta n(t)}{dx}} \quad (1.22) \]

Where \( \Delta n(t) \) represents the time dependent values of excess carrier density and \( G \) is the photo generation rate.

According to equation 1.21, low effective masses of electrons and holes are required to obtain high diffusion mobilities and therefore high diffusion coefficients. This information is needed to calculate the diffusion length of the minority charge carrier the average
distance that the minority charge carrier transports starting from its generation until it recombines. It is a key parameter to judge the photocatalytic activity of a certain material. Ideally, large diffusion lengths are needed so that the minority charge carrier can reach the surface without being recombined. It is denoted by (Lₙ) for electrons in p-type semiconductor and (Lₚ) for holes in n-type semiconductor that is defined by the equation below:

\[ L_n = \sqrt{D_n \tau_n}, \quad L_p = \sqrt{D_p \tau_p} \]  

(1.23)

Where Dₙ and Dₚ are the diffusion coefficients for electrons and holes respectively and \( \tau_n \) and \( \tau_p \) are the lifetimes of electrons and holes respectively.

The crystal structure and the electronic band structure greatly affect the transport properties. Experimentally, the carrier mobility is deduced from resistivity and charge carrier concentration measurements through the van der Paw technique with the Hall measurement.\(^{62,63}\)

Recently, DFT calculations have provided important information about the carrier mobility that can be deduced from the electronic band structure. A large band width in the conduction band and valence band reflects high carrier mobility of the electrons and holes respectively. Two factors increase the mobility: the first is the increase in the width of the band and the second is the extensive mixing and hybridization between the orbitals of nearby atoms. Consequently, the enhanced overlap between the orbitals increases the bandwidth and results in better transport properties. From DFT calculations, the dispersion curve is a powerful tool to infer the transport properties. The curvature of the dispersion curve reflects the carrier effective masses through the following equation (1.24):
\[
\frac{d^2E}{d^2k} = \frac{\hbar^2}{m}
\]  
(1.24)

Therefore, highly parabolic curves indicate smaller effective masses.

Charge recombination is one of the detrimental factors for the activity of the photocatalyst. Upon recombination the free carriers are lost when an excited electron from the conduction band recombines with a hole from the valence band. Since the carrier mobility decreases with doping concentration, highly crystalline and pure semiconductors are needed to minimize the recombination processes. Three types of recombination process are generally defined:

1) the band to band recombination which is the main recombination process in the direct band gap semiconductor

2) Shockley-Read Hall recombination which is dominant in indirect semiconductors and in materials that contain defect states.\textsuperscript{64,65} The surface of the semiconductor and grain boundaries act as trap sites for the free charge carriers.

3) Auger recombination which is similar to band-to-band recombination however an additional particle is excited through additional energy.\textsuperscript{66}

In powder semiconductors, the diffusion process controls the transport properties of the free charge carriers. Hence, the charges need to be directed separated along different crystallographic directions or with the help of modification of the interface between the semiconductor/ metal and semiconductor/electrolyte interface. These ideas will be discussed in the following section.
Carrier transport at semiconductor/surface interface

So far, the path of the charge carriers have been through the bulk of the semiconductor. Assuming that these processes were successful, the charge carriers need to be transported to the active sites of the surface or to cocatalyst so that they undergo redox reactions. To improve efficiency, a driving force for charge carriers must be created through surface modifications such as creating new electronic structures on the surface. Therefore, the interface of the semiconductor with the electrolyte-semiconductor, or metal is vital to enhance the charge separation through band bending.

![Scheme of the band bending at a semiconductor/electrolyte interface before (a) and after equilibrium (b).](image)

Figure 1.6 Scheme of the band bending at a semiconductor/electrolyte interface before (a) and after equilibrium (b).
The principle of band bending is well known in semiconductor physics and involves the formation of a built-in potential or space charge upon the contact of the semiconductor with electrolyte or with metal.\(^5^9\) In the field of particle photocatalysis, one of the most frequently used configuration is that of an \(n\)-type semiconductor particle with metal nanoparticles on its surface immersed in an electrolyte. In this case two interfaces must be discussed:

First, the semiconductor/electrolyte and the semiconductor/metal interfaces. In terms of band bending, there is a similarity in the behavior of the particle in contact the electrolyte and metal. Figure 1.6. represents the band bending that occur between semiconductor/electrolyte interfaces.

When a semiconductor particle is immersed in the solution, the fermi level in the semiconductor (\(E_F\)) will equilibrate with the redox potential of the electrolyte (\(E_0\)) while keeping the band edges pinned. The equilibrium is achieved by the transfer of the electrons from the semiconductor into the electrolyte. Hence, the electrons are depleted in the region of contact with electrolyte, referred the space charge layer or depletion layer.

The band bending is described by Poisson’s equation with the assumption of a one-dimensional infinite interface.

\[
\frac{d^2 \psi(x)}{dx^2} = -\frac{eN_D}{\varepsilon_r \varepsilon_0} \quad 0 \leq x \leq W
\]

(1.25)

Where \(W\) is the depletion layer thickness, \(N_D\) is the majority carrier density, \(\varepsilon_r\) and \(\varepsilon_0\) are the relative dielectric constant of the semiconductor and the vacuum permittivity
respectively.55 Solving the equation for boundary conditions for an $n$-type semiconductor $(0 \leq x \leq W)$;

$$\psi(x) = -\frac{eN_D}{\epsilon_i \epsilon_r} \left(Wx - \frac{1}{2}x^2\right) - (E_D - E_{FB})$$

(1.26)

Then

$$W = \sqrt{\frac{2\epsilon_0 \epsilon_r V_B}{qN_d}}$$

(1.27)

Where $e$ is the elementary charge, $V_B$ is the potential drop in the space-charge layer which can be defined as the potential barrier height that the majority carriers should overcome so that they can transfer to the solution.

As discussed earlier, the band edge position is one of the important characteristics of a photocatalyst. It determines whether the semiconductor is thermodynamically capable of driving the water splitting reaction. The flat band potential is a term that describes the intrinsic band edge of the majority carriers in the absence of band bending i.e. when the band becomes flat. Assuming the surface states do not affect the flat band potential, the majority band edge can be estimated using the Mott-Schottky measurements.68 The Mott-Schottky equation applies only in the double layer region of the semiconductor where no faradaic currents are measured. Hence, the capacitance $C$ is related to flat band potential and the majority carrier concentration $N_D$ through the following equation:

$$\frac{1}{C^2} = \frac{2}{eA^2 \epsilon_r \epsilon_0 N_D} (E_{app} - E_{FB} - \frac{k_B T}{e})$$

(1.28)
$E_{app}$ is the applied potential. Hence, plotting the $1/C^2$ vs. the potential shows in a straight line with a slope $= \frac{k_BT}{eA^2\varepsilon_e\varepsilon_0N_A}$ and intercept of flat band potential $E_{FB}$.

The bare surface of semiconductor photocatalysts have often been reported as being inactive, requiring the addition of a cocatalyst. The presence of a cocatalyst on the surface creates a modified electronic structure at the metal-semiconductor interface.\textsuperscript{69} The nature of the interface largely dependent on the type of the semiconductor (n or p type) and the position of the fermi level in the semiconductor ($\phi_{SC}$) versus the work function of the metal $\phi_m$. Detailed derivation of the metal-semiconductor interface is described elsewhere.\textsuperscript{70}

Briefly there are two types of interfaces. The first involves the formation of a Schottky barrier which is generally unfavorable for electron transfer. This type of barrier occurs in case where $(\phi_{SC_n}) < \phi_m$ or $\phi_m < \phi_{SC_p}$. However, an energetically favorable interface, "ohmic contact" is formed when $(\phi_{SC_n}) > \phi_m$ or $\phi_m > \phi_{SC_p}$ in which case an accumulation layer is formed on the surface.

As mentioned earlier, this modified interface generally creates a built-in potential. The diffusion voltage, $V_D$ is defined by:

$$eV_D = |\phi_m - \phi_{SC}|$$

(1.29)

Where the maximum Schottky barrier height that need to be overcomed is described by the work function of the metal:

$$\phi_B = |\phi_m - \chi_{SC}|$$

(1.30)
The surface states commonly present on the surface affects the height of the barrier. This is generally described by the Bardeen limit which is described in detail elsewhere.\textsuperscript{71}

The cocatalyst is indispensa
\[T\]ble to create the driving force of the charge carriers through the formation of the described interfaces. One important factor is the cocatalyst size which should be taken to consideration to attain the optimal efficiency. The cocatalyst is the active site of the electrochemical reactions therefore it is crucial parameter to optimize overall efficiency.

**Catalytic efficiency and mass transfer**

Upon the successful achievement of all the previously reported photophysical and photochemical processes, utilizing an efficient cocatalyst will result into productive photocatalytic water splitting in the visible light. The ideal electrocatalyst must exhibit the minimum overpotential when transferring the electrons and holes to the appropriate reactants to drive reduction and oxidation half reactions respectively. The mode of action of the cocatalyst is still controversial between acting as active sites for the redox reactions or also accelerating the consumption of holes. The overall water splitting is composed of two half reactions:

The reduction half reaction starting either from hydronium ions or water at 0 V vs. RHE:

\[2H^+ + 2e^- \rightarrow H_2 \quad \text{(acid)} \quad \text{or} \quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{(base)} \quad (1.31)\]

The oxidation half reaction starting from water or hydroxyl ions as reactants at 1.23 V vs. RHE

\[2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad \text{(acid)} \quad \text{or} \quad 4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad \text{(base)} \quad (1.32)\]
It was reported that the hydronium ions are easier to reduce than water molecules, and hydroxyl ions are more easy to oxidize than water molecules.

The rate of the electrochemical reactions that occurs on the surface of the cocatalyst are driven by the potential shift through previously discussed photo physical processes. Only if this potential can be measured, then the rate can be separately determined through electrochemical approaches. The electro catalytic activity is generally described using the Tafel equation by considering only the forward reaction. The reaction rate (r) of the photo electrochemical half reactions:

\[
r = \frac{i_0}{nF} \exp\left(\frac{\alpha nF(E_D - E^0)}{RT}\right)
\]

Where \(i_0\) is the exchange current of the given metal (A), \(\alpha\) is the transfer coefficient, \(n\) is the number of electrons exchanged, \(F\) is the Faraday constant, \(E_D\) and \(E^0\) are the fermi level of the metal and redox potential in the solution, respectively, \(R\) is the universal gas constant, and \(T\) is the absolute temperature.

Many research efforts have been focused towards developing a criteria to identify efficient cocatalysts using electrochemical approaches. For hydrogen evolution, the volcano plot which represents the current density versus the free energy of hydrogen adsorption on different metals showed that there is an optimal value for the free energy. For oxygen evolution, a similar approach was done for metal oxides versus several thermodynamic descriptors.

In order to minimize the use of noble metals which are rare and costly, several approaches have been adopted. Some examples include depositing islands of cobalt or nickel on the
metal surface,\textsuperscript{79} mixed oxyhydroxides (e.g. nickel-iron) and perovskites as low over potential cocatalysts.\textsuperscript{80-83}

So far the three main components of the photocatalyst have discussed; i.e. the semiconductor, semiconductor/electrolyte (or metal), and the interface. However, it is important to emphasize the role of thermodynamic and kinetic information including the mass transfer of the reactants. The pH of the solution greatly affects the nature and the concentration of the reactants. For a particulate photocatalyst, there is no pH gradient since H\textsubscript{2} and O\textsubscript{2} are generated in same compartment which minimizes the activity loss in the reactor.\textsuperscript{84} The effect of pH has been studied extensively from an electrochemical point of view in which it was found to greatly affect the mechanism of oxygen and hydrogen evolution but there is limited information about the effect of electrolyte is on photocatalytic overall water splitting.\textsuperscript{54,85}
1.3. Towards visible responsive water splitting: Strategies

Having discussed the photo physical and photochemical processes that govern photocatalytic overall water splitting, it is obvious that developing the efficient visible responsive semiconductor material is indeed challenging. The water splitting reaction is thought to be the “holy grail” of chemistry. To sum up, the requirements that must be fulfilled by the ideal photocatalyst are summarized below.

1) The Band gap energy and band positions: To meet the benchmark STH 10% efficiency, the semiconductor must possess extended absorption of the visible light to around 600 nm which corresponds to around 2.0 eV. In addition, the band edges must straddle the water reduction and oxidation potentials, i.e. the conduction band must be more negative than the hydrogen evolution potential and the valence band must be more positive than the oxygen evolution potential. This is extremely important because although some semiconductors have satisfied the band gap requirements described earlier, they have unsuitable band positions for either hydrogen evolution (e.g. WO₃ and Fe₂O₃) or water oxidation.

2) Stability of the semiconductor material under the reaction conditions. The metal chalcogenides (CdS and CdSe) satisfy the band gap and band edge requirements, yet they are unstable in the water oxidation. This is due to the presence of S²⁻ and Se²⁻ which exhibit more positive oxidation potential than water, driving their self-oxidation and photo degradation. Their instability limited their efficiency for overall water splitting.
3) The material must exhibit high crystallinity with minimal defect states in order to minimize the recombination processes and increase the carrier lifetime as described earlier. Furthermore, the photocatalyst must possess high activity for hydrogen and oxygen evolution as described in the previous section.

4) The constituent elements of the semiconductor material must be abundant cheap and environmentally friendly and the synthesis methods should be facile and largely scalable

Since the seminal work of Honda and Fujishima in 1972, much efforts has been used to study the TiO\textsubscript{2} and other titanium based semiconductors such as SrTiO\textsubscript{3}, Na\textsubscript{2}TiO\textsubscript{13}, BaTi\textsubscript{4}O\textsubscript{9}, CaTiO\textsubscript{3}, K\textsubscript{2}La\textsubscript{2}Ti\textsubscript{4}O\textsubscript{10} and La\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} Until the middle of the 1980s, numerous successful photocatalysts successfully performed overall water splitting, but under UV radiation. These effective photocatalysts are based on transition metal cations with either empty d orbitals (d\textsuperscript{0}) electronic configurations such as Ti\textsuperscript{4+}, Zr\textsuperscript{4+}, Nb\textsuperscript{5+}, Ta\textsuperscript{5+} and W\textsuperscript{6+} or filled d orbitals i.e. d\textsuperscript{10} configuration with examples of Ga\textsuperscript{3+}, In\textsuperscript{4+}, Ge\textsuperscript{4+}, Sn\textsuperscript{4+}, and Sb\textsuperscript{5+}. High quantum efficiencies have been achieved reaching 56\% at 270 nm with La doped NaTaO\textsubscript{3} photocatalyst. Many factors have been studied to increase the efficiency of these photocatalysts such as the effect of morphology on creation of active sites, the effect of distortion of the framework on the energy structure, and the effect of the elements contributing to the valence bands. Examining the electronic structure of the effective photocatalysts, it was observed that the lowest unoccupied molecular orbitals (LUMO) is determined by the d\textsuperscript{0} or d\textsuperscript{10} transition metal cation which is generally higher than the hydrogen evolution potential. However, the valence band is mainly determined by the O 2p orbitals which are generally located around
3.0 eV. This indicates that these classes of photocatalyst must have a band gap of at least 3.0 eV.\textsuperscript{120} Therefore, since the conduction band cannot be lowered, band gap engineering is necessary to minimize the band gap and shift the absorption into the visible region. Several approaches have been adopted which can be summarized by Figure 1.7 below:\textsuperscript{128}

Figure 0.7 A conceptual image of the band structures for photocatalysts with visible response. Adapted from K. Takanabe.\textsuperscript{128}

1) Doping; either with d1-d9 metals or with heteroatoms such as C, N, P, S,Se

2) Formation of solid solutions; starting with two semiconductors with similar crystal structure

3) Valence band engineering of the d0 or d10 transition metals by the formation of (oxy)nitride/(oxy sulfide) or the incorporation of s2d10 metals;
1.3.1. Formation of solid solution

The state of the art efficiency for visible overall water splitting was achieved by GaN:ZnO solid solution with Rh$_{2-x}$Cr$_x$O$_3$ as cocatalyst reaching 5.9% quantum efficiency.$^{130}$ This solid solution is composed of two UV active semiconductors; the GaN ($E_g=3.4$ eV) and ZnO ($E_g=3.2$ eV) with similar crystal structure and lattice parameters.$^{123,133}$ The visible response of the resultant solid solution is explained by the contribution of the Zn 3d atomic orbitals to the valence band, where bonding between Zn and N atoms is created due to the formation of the solid solution. Due to the large overlap between the ZnO and GaN electronic structures, the Zn to Ga excitation is utilized. This approach proved to be promising to tune the band gap and the band edge positions by modifying the composition.$^{133}$

1.3.2. Doping

Doping is a conventional method used to obtain visible-responsive photocatalysts including UV-responsive oxides. It is defined by the replacement of a metal cation from the crystal lattice with a foreign element which may be d$^1$-d$^9$ transition metals$^{134-141}$ with partially filled d orbitals or with anions such as C$^{4-}$, N$^{3-}$, or S$^{2-}$.$^{142-144}$ Although this method successfully turns the white UV responsive powders into colorful visible responsive photocatalysts, it is detrimental for the photocatalytic activity of the material. This is due to the formation of the discrete energy states in the forbidden band gap which act as recombination centers for charge carriers. The dopants create localized energy levels
instead of a complete band. It is crucial to differentiate between the energy gap created by the impurity level and the intrinsic band gap.

One of the main problems of doping is the difficulty to control the charge balance which creates additional oxygen vacancies acting as recombination centers. The co-doping approach seemed to be effective to obtain visible responsive photocatalysts. SrTiO$_3$ was doped utilizing Cr$^{3+}$/Ta$^{5+}$, Cr$^{3+}$/Sb$^{5+}$, Ni$^{2+}$/Ta$^{5+}$ and doping with Rh while TiO$_2$ have extensively studied for co-doping with Cr$^{3+}$/Sb$^{5+}$, Rh$^{3+}$/Sb$^{5+}$, Ni$^{2+}$/Nb$^{5+}$. When dopants are introduced into the lattice of the host material (SrTiO$_3$, TiO$_2$), they create electron donor levels. The importance of co-doping by Ta$^{5+}$, Sb$^{5+}$ and Nb$^{5+}$ is to compensate the charge imbalance created by the substitution of Ti$^{4+}$ by lower oxidation state metals such as Cr$^{3+}$ or Ni$^{2+}$ and hence suppress the formation of recombination centers. Rh doped STO exhibited hydrogen evolution activity from aqueous methanol and TiO$_2$ co-doped with Rh/Sb showed oxygen evolution activity from solution of silver nitrate.

Doping TiO$_2$ with non-metal dopants such as C and N successfully creates visible responsive photocatalysts.$^{142-144}$ However, it creates additional charge recombination sites by the formation of localized electronic densities.$^{145}$

Eventually, it seems that the doping method is disadvantageous due to the formation of the recombination centers which decrease the mobility of electrons and holes. Hence, complete valence band hybridization need to be developed instead.
1.3.3. Valence band engineering

Valence band engineering of the UV responsive metal oxides is one of the promising strategies to create a visible responsive photocatalyst. It involves the contribution of additional element into the top of the valence band and shifting the band edge towards more negative potential and hence minimizing the band gap. This method creates a complete valence band which ensures the smooth flow of the holes and minimizes recombination in comparison to doping.

Two main approaches have been adopted; the first includes the formation of (oxy) nitrides or (oxy) sulfides.\textsuperscript{146-154} In this approach, the additional N or S provides 2p and 3p orbitals respectively which have higher energy level than the oxygen 2p orbitals. This created a new valence band with concrete electronic structure and narrower band gap. The partial or full nitridation of the large band gap Ta\textsubscript{2}O\textsubscript{5} (3.9 eV) results into visible TaON (2.4 eV) and Ta\textsubscript{3}N\textsubscript{5} (2.1 eV) respectively.\textsuperscript{146-152} These two materials have proven to evolve both hydrogen and oxygen using sacrificial agents.\textsuperscript{150} Furthermore, the characterization of the band edges suggest that both are suitable for overall water splitting reaction. Nonetheless, the material are greatly affected by the experimental parameters of the high temperature nitridation process.

The second approach is to incorporate transition metals with s\textsuperscript{2}d\textsuperscript{10} electronic configuration.\textsuperscript{155-163} A new valence band above the O2p band is created by the orbitals of Pb 6s in Pb\textsuperscript{2+},\textsuperscript{164,165} Bi 6s in Bi\textsuperscript{3+},\textsuperscript{166} Sn 5s in Sn\textsuperscript{2+},\textsuperscript{167} and Ag 4d in Ag+.\textsuperscript{168} Lead based semiconductors have been reported such as PbMoO\textsubscript{4},\textsuperscript{169} RbPb\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10},\textsuperscript{164} PbBi\textsubscript{2}Nb\textsubscript{2}O\textsubscript{9} showing both hydrogen and oxygen evolution activity in the visible
region. However, the toxicity of lead is disadvantageous which limits the research into lead based materials.

Silver based materials are environmentally friendly. Several photocatalysts also showed oxygen evolution using sacrificial reagents for Ag$_3$VO$_4$, Ag LiSn$_{2/3}$O$_3$, and Ag LiSn$_{2/3}$O$_3$ and most importantly AgNbO$_3$ which showed activity for both hydrogen and oxygen using sacrificial reagents. However, the presence of silver increases the cost of the photocatalyst.

Many bismuth based material have shown to evolve both hydrogen and oxygen under UV radiation most importantly Bi$_2$Ti$_2$O$_7$, Bi$_{12}$TiO$_{20}$, Bi$_4$Ti$_3$O$_{12}$, BaBi$_4$Ti$_4$O$_9$, and Bi$_3$TiNbO$_9$. Moreover, large family of bismuth based visible responsive photocatalysts have been reported mainly for oxygen evolution activity. These include Bi$_2$WO$_6$, Bi$_2$MoO$_6$, Bi$_2$Mo$_3$O$_{12}$, BiCu$_2$VO$_6$, BiZn$_2$VO$_6$, and the highest oxygen evolution is achieved by BiVO$_4$. BiVO$_4$ is one of the promising material for oxygen evolution although material is not suitable for H$_2$ evolution, yet it proved to be successful in Z-scheme. BiVO$_4$ has been extensively studied by DFT calculations to understand the electronic structure and the superior activity for oxygen evolution. The valence band of BiVO$_4$ was confirmed to be composed for Bi 6s orbitals, whereas the conduction band is composed d$^0$ orbitals. The main limitation of BiVO$_4$ is the unsuitable conduction band edge position for hydrogen evolution.

Tin based semiconductors have shown interesting visible responsive absorption such as Sn$_2$TiO$_4$, SnWO$_4$ and SnNb$_2$O$_6$. However, only Sn$_2$Nb$_2$O$_6$ showed activity for both hydrogen and oxygen using sacrificial reagents whereas only SnWO$_4$ has been reported as a photoanode. It is noteworthy that DFT calculations also showed 5s orbitals
of Sn$^{2+}$ contribute to the valence band in the SnNb$_2$O$_6$, Sn$_2$Nb$_2$O$_7$, SnTa$_2$O$_6$, and Sn$_2$Ta$_2$O$_7$.\textsuperscript{167,187,188} The main challenge of the Sn$^{2+}$ based material is the metastable state nature of Sn$^{2+}$ and the oxidation into Sn$^{4+}$ which acts as a recombination centers.\textsuperscript{188} Therefore, to increase the efficiency of the photocatalyst, it is important to understand the crystal and electronic structure of the Sn$^{2+}$ material with the help of DFT calculations. In addition to that, the synthesis methods must be carefully chosen to minimize the oxidation of Sn$^{2+}$ while maintaining high crystallinity material.

1.4. Scope of the Thesis

As discussed earlier, the main challenge is to develop a suitable photocatalyst for visible overall water splitting reaction. To achieve a “photocatalyst by design”, fundamental understanding of the photo physical and photochemical processes is inevitable. Indeed, a systematic criteria to characterize the parameters that affect the overall efficiency is necessary. Being able to determine the “Achilles’ heel” of the semiconductor photocatalyst, opens the door not only to enhancing the efficiency of current efficient semiconductors but also to designing novel semiconductor material.

This thesis focuses on the synthesis and characterization of Sn$^{2+}$-based and Bi$^{3+}$-based material as promising photocatalysts. This work has two directions:

1) To provide a systematic protocol to study of the optoelectronic properties using a combination of experimental methods and theoretical calculation. (Chapter 2 and 4).
2) To investigate the effect of the synthesis method on the crystal structure and photocatalytic activity of Sn$^{2+}$ based photocatalyst. The flux-assisted method was investigated as a promising route to enhance the activity of SnNb$_2$O$_6$ for hydrogen evolution reaction (chapter 3) and hydrothermal method as novel method to synthesize SnSbO$_6$ and study in detail the crystal structure (chapter 5).

In chapter 2, a combination of experimental and computational methods was applied to investigate the crystal structure and optoelectronic properties of a series of bismuth titanate material; the pyrochlore, sillenite, and perovskite-like structures. The study revealed that the non-stoichiometric Bi$_{2-x}$Ti$_2$O$_{7-1.5x}$ structure ($x = 0.25$) is experimentally obtained with a clear distinction between this material and the ideal perfect stoichiometric configuration ($x = 0$) was observed. The calculated results for the band gap and absorption coefficient revealed a UV absorption for the three structures. The calculated band gap of the non-stoichiometric structure Bi$_{1.75}$Ti$_2$O$_{6.62}$ exhibited excellent agreement with the band gap of 3.3 eV measured via ellipsometry, which is narrower than the band gap computed for the stoichiometric Bi$_2$Ti$_2$O$_7$ material (3.6 eV). The sillenite and perovskite structure showed a calculated band gaps of 3.1 and 3.6 respectively. The nature of the band gap was found to be direct for the pyrochlore and sillenite and indirect for the perovskite. The calculated static dielectric constants exhibited high values of up to 80.1 for Bi$_{1.75}$Ti$_2$O$_{6.62}$, 31.2 for the Bi$_{12}$TiO$_{20}$ and 57.1 for the Bi$_4$Ti$_3$O$_{12}$. These high dielectric constants reflect excellent charge separation of these material. Relatively high effective electron and hole masses in certain directions were found for the non-stoichiometric pyrochlore structure, which may result in lower charge carrier mobility. However, low electron and hole effective masses were observed for the sillenite and
perovskite like structures. The values of the effective masses was lower than TiO$_2$ which indicate their excellent transport properties. The most prominent difference is that the flat band potential of the three structures is more negative than that of the TiO$_2$ which may have various potential applications, e.g., may be substituted for or mixed with TiO$_2$ is dye-sensitized solar cells and photocatalytic applications.

In chapter 3, the role of flux-assisted synthesis using a molten salt has been investigated as a means to control the surface properties. The crystal morphology was successfully tuned by increasing the flux to reactant molar ratio, which afforded defined particles with non-aggregated surfaces. The XRD patterns and SEM analyses confirmed a 2D anisotropic growth along the bc plane, providing a plate-like morphology as the flux ratio increased. The photocatalytic activity for hydrogen evolution was enhanced as the flux ratio was increased, reaching the highest value at a 1:10-F ratio. This result was explained by the beneficial role of increased flux in allowing the formation of tin niobate at a lower reaction temperature compared with solid-state synthesis. This heightened activity coincides with the minimized amount of Sn$^{4+}$ on the surface boundaries, which may act as trap states.

In chapter 4, the synthesize the α and β SnWO$_4$ using flux assisted method was attempted and β-SnWO$_4$ was successfully synthesized at lower temperature than the solid state synthesis which was reported previously. The absorption properties of the powdered showed a band gap of 2.05 and 2.9 eV for the α and β SnWO$_4$, respectively. The narrow band gap of α SnWO$_4$ was interesting to perform a combined experimental and theoretical approach which was used to determine the photo physical properties of α-
SnWO$_4$. These properties include the band gap, absorption coefficient, dielectric constant, and charge carrier effective masses. All of the measured and calculated properties are in excellent agreement. Despite the fact that α-SnWO$_4$ presents interesting absorption properties and efficient charge carriers extraction, it suffers from weak transport properties such as high effective masses, which may explain the low PEC performance. The methodology presented in this study provides an excellent tool to deeply understand the photo electrochemical performance of various materials at high accuracy.
1.5. References


A Combined experimental–theoretical study of the optoelectronic properties of non-stoichiometric pyrochlore bismuth titanates

A combination of experimental and computational methods was applied to investigate the crystal structure and optoelectronic properties of the non-stoichiometric pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_{7-1.5x}$. The detailed experimental protocol for both powder and thin-film material synthesis revealed that a nonstoichiometric $\text{Bi}_{2-x}\text{Ti}_2\text{O}_{7-1.5x}$ structure with an $x$ value of ~0.25 is the primary product, consistent with the thermodynamic stability of the defect-containing structure computed using density functional theory (DFT). Furthermore, the sillenite ($\text{Bi}_{12}\text{TiO}_{20}$) and the perovskite-like ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) structures were also synthesized by same approach and their optoelectronic properties were predicted by DFT calculations. The approach of density functional perturbation theory (DFPT) was used along with the standard Perdew-Burke-Ernzerhof functional (GGA PBE) and the screened Coulomb hybrid Heyd-Scuseria-Ernzerhof (HSE06) functional, including spin–orbit coupling, to investigate the electronic structure, the effective electron and hole masses, the dielectric constant, and the absorption coefficient. The crystal structure was experimentally studied using Rietveld refinement. The calculated values for these properties are in excellent agreement with the measured values, corroborating the overall analysis. These compounds

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1 This chapter was adapted from:
show low exciton binding energy, high dielectric constants and low effective hole and electron masses in one crystallographic direction at least indicating good charge separation and carrier transport properties, respectively. This study indicates potential applications of bismuth titanate as a wide-band gap material, e.g., as a substitute for TiO\textsubscript{2} in dye sensitized solar cells and UV-light-driven photocatalysis.

2.1. Introduction

Heterogeneous Semiconductors lie at the heart of optoelectronic technology, functioning as photon absorbers and/or as charge-carrier transporters. TiO\textsubscript{2} is one of the most popular semiconductors for this purpose; it has been utilized in dye-sensitized solar cells\textsuperscript{1} and in basic studies of photo electrochemical water splitting reactions.\textsuperscript{2} To improve the performance of TiO\textsubscript{2}-based devices, alternative semiconductor materials with highly effective photophysical properties, such as light absorption, charge carrier extraction and carrier diffusion, are currently screened.

Among the most promising materials are bismuth titanates family which include Bi\textsubscript{2}Ti\textsubscript{4}O\textsubscript{11},\textsuperscript{3} Bi\textsubscript{8}TiO\textsubscript{14},\textsuperscript{4} Bi\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7},\textsuperscript{5} Bi\textsubscript{12}TiO\textsubscript{20}, and Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12}.\textsuperscript{6} They demonstrate great potential because of their excellent photo physical properties and their band gaps, which can be tuned through site substitution with different elements.\textsuperscript{7} In particular, the bismuth titanate pyrochlore structure, sillenite and perovskite-like aurivillus structure have been applied in various applications. Most importantly, in the field of photocatalysis where they have been used as UV-light-responsive photocatalyst to degrade organic pollutants.\textsuperscript{8-17} In addition to that, the pyrochlore has been used as a pigment\textsuperscript{18} the sillenite in holographic
interferometry, and the perovskite-like structures in field of nonvolatile ferroelectric random access memories (FRAMS).

In the literature, the properties and functions of bismuth titanates remain controversial because of a lack of detailed information on their optoelectronic properties. The crystal and electronic structure dictate these properties. In part, this lack of clarity results from the difficulty in controlling their chemical stoichiometry through material synthesis. This in part can be explained by the complexity of the phase diagram.

The synthesis of these three structures have been extensively studied using many synthesis methods resulting in several morphologies such as nanowires, nanotubes, and hierarchical assemblies which have been reported as photoactive materials.

Pyrochlore bismuth titanate has been synthesized using several methods, including metal–organic decomposition, the sol–gel method, and co-precipitation. It was first introduced as Y$_{1-x}$Bi$_x$Ti$_2$O$_7$, and several non-stoichiometric forms have also been reported, such as the Bi$^{3+}$ and O$^2-$ deficient compound Bi$_{1.833}$Ti$_2$O$_{6.75}$. Often, the perovskite Bi$_3$Ti$_5$O$_{12}$ structure is co-generated in the attempt to synthesize the stoichiometric pyrochlore Bi$_2$Ti$_2$O$_7$ through solid-state reactions. Later, Bi$_{1.74}$Ti$_2$O$_{6.62}$ synthesized via co-precipitation was reported as a single pure product refined via neutron diffraction, thereby confirming the stoichiometry. Recently, a non-stoichiometric structure synthesized via an aqueous sol–gel method was reported, namely, a non-stoichiometric (Bi$_{2-x}$Ti$_{0.75x}$)Ti$_2$O$_7$ material with $x$ equal to 0.44.
Although these materials have been thoroughly studied experimentally, there remains a need for a detailed study to elucidate the crystal structure as well as the optical and transport properties of the nonstoichiometric $\text{Bi}_{2-x}\text{Ti}_2\text{O}_{7-1.5x}$, $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

To resolve the inconsistencies regarding the crystal structure and optoelectronic properties of these series of bismuth titanate in the literature, a detailed study combining both experimental and theoretical methods is reported. On the experimental side, care was taken to synthesize the pure phase without any secondary phases. Density functional theory (DFT) and density functional perturbation theory (DFPT) employing both the standard PBE functional and the more accurate screened Coulomb hybrid HSE06 functional were employed with the inclusion of spin–orbit coupling. This approach enabled the determination of the electronic structure, optical absorption coefficient, dielectric constant and effective charge-carrier masses of the non-stoichiometric $\text{Bi}_{1.75}\text{Ti}_2\text{O}_{6.62}$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Bi}_{12}\text{TiO}_{20}$. There was good agreement between the measured and the calculated values. The impact of the non-stoichiometric structure relative to the ideal $\text{Bi}_2\text{Ti}_2\text{O}_7$ stoichiometric structure on these properties was also investigated, and a general comparison of the properties with those of the well-studied material TiO$_2$ was performed.

2.2. Results and discussion

2.2.1. Crystal structure

An experimental attempt was done to synthesize the single phases of a series of bismuth titanate semiconductors with pyrochlore, sillenite, and perovskite structures. The co-precipitation method was used to synthesize powder materials with various Ti/Bi
precursor ratios for the pyrochlore, Bi/Ti=12 for sillenite, and Bi/Ti=1.3 for the perovskite. For the pyrochlore structure, samples with starting Ti/Bi molar ratios of 1, 1.23, 1.5, 1.75 and 2 were synthesized. The actual Ti/Bi ratios in these samples were confirmed via inductively coupled plasma (ICP) and found to be 0.96, 1.16, 1.51, 1.71 and 1.92, respectively. Figure 2.1a shows the XRD patterns for the samples with varied Ti/Bi molar ratios. Figure 2.1b shows a magnified view of the region in which amorphous phases appear (23° < 2θ < 28°). It can be seen that for the sample with an initial Ti/Bi ratio of 1, a mixture of the pyrochlore phase with Bi₄Ti₃O₁₂ as a secondary phase was obtained at 2θ = 33°. The XRD pattern of the powder sample with a Ti/Bi ratio of 1.16 showed a single phase of the pyrochlore structure with no impurities (neither a secondary nor an amorphous phase), and the peaks were indexed according to ICSD PDF# 01-089-4732.
Figure 2.1 A) XRD patterns of the powder samples prepared with different Ti/Bi ratio of (a) 1, b) 1.23, c) 1.50, d) 1.75, e) 2.00. B) The magnified XRD patterns where the amorphous phases and the Bi$_4$Ti$_3$O$_{12}$ secondary phase (asterisk) are observed.

The characteristic peaks of the pyrochlore structure were clearly observed for the (111) and (222) peaks. Indeed, no amorphous phase existed for the samples with Ti/Bi ratios of 1.16 to 1.51. Higher Ti/Bi ratios of 1.72 and 1.92 led to the formation of an amorphous phase that manifested as a broad increase in the background at 2θ values of 23 to 32°. This chemical composition was confirmed by an ICP measurement, in which a Ti/Bi ratio of 1.16 was found, close to the initial ratio of 1.23. This confirmed that excess titanium created vacancies at the bismuth and oxygen sites, consistent with the proposal in the
literature that such vacancies may stabilize the entire structure.\textsuperscript{26} It should be noted that the impurity phase with low Ti (Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12}) caused the band edge to shift to longer wavelengths, whereas excess Ti would not cause any shift in the band edge, as observed from the Kubelka–Munk function from the UV-Vis spectroscopy results.

Therefore, for the subsequent characterizations presented in this work, a ratio of Ti/Bi = 1.16 was chosen. Figure 2.2 (A) shows the representative XRD patterns for (a) the single-phase Bi\textsubscript{2-x}Ti\textsubscript{2}O\textsubscript{7-1.5x} powder synthesized using the co-precipitation method, to be refined using the Rietveld analysis method; (b) the Bi\textsubscript{2-x}Ti\textsubscript{2}O\textsubscript{7-1.5x} thin film deposited on a Si substrate, used for ellipsometric spectroscopy; and (c) the Bi\textsubscript{2-x}Ti\textsubscript{2}O\textsubscript{7-1.5x} thin film deposited on an FTO substrate, used for Mott–Schottky analysis.
Figure 2.2. A) XRD patterns (A) of (a) Bi$_{1.75}$Ti$_2$O$_{6.62}$ powders, (b) a Bi$_{1.75}$Ti$_2$O$_{6.62}$ thin film on a Si substrate, and (c) a Bi$_{1.75}$Ti$_2$O$_{6.62}$ thin film on an FTO substrate. * FTO B) XRD patterns of Bi$_{12}$TiO$_{20}$ and Bi$_4$Ti$_3$O$_{12}$ and films of FTO, and powders that were synthesized using the co-precipitation method.

The thin film on the Si sample was calibrated versus the Si (400) peak, which appears at $2\theta = 69.12^\circ$. All of the samples exhibited a single-phase pyrochlore structure with the same d-spacing for the main peaks (e.g., $d_{222} = 2.98$ Å). The relative intensities of the peaks were similar to those in the powder samples, thereby confirming that the films were randomly oriented, similar to the polycrystalline powders.

Rietveld analysis was performed for the Bi$_{2-x}$Ti$_2$O$_{7-1.5x}$ sample with Ti/Bi = 1.16 synthesized using the co-precipitation method. The Wyckoff positions of the atoms are summarized in Table 2.1, and the lattice parameters are summarized in Table 2.2.

Table 2.1. The atomic positions and occupancy for bismuth, Titanium, and oxygen atoms in BiTiO-1.23 sample refined by Rietveld analysis.

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>96</td>
<td>0.0000</td>
<td>-0.02846</td>
<td>0.02846</td>
<td>0.1463</td>
</tr>
<tr>
<td>Ti</td>
<td>16</td>
<td>0.5000</td>
<td>0.5000</td>
<td>0.5000</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>48</td>
<td>0.1250</td>
<td>0.1250</td>
<td>0.43297</td>
<td>1</td>
</tr>
<tr>
<td>O’</td>
<td>8</td>
<td>0.1250</td>
<td>0.1250</td>
<td>0.1250</td>
<td>0.624</td>
</tr>
</tbody>
</table>
The sample had a cubic structure belonging to the Fd3m space group and a lattice parameter of \( a = 10.35 \) Å. Bismuth ions (\( \text{Bi}^{3+} \)) partially occupied 96g, which is of lower symmetry than the normal atomic position (16c) in this space group. Titanium ions (\( \text{Ti}^{4+} \)) fully occupied the 16d position, and two types of oxygen atoms were present, the first (O) fully occupying the 48f position and the second (O’) partially occupying the 8a position. From Table 2.1, the numbers of bismuth, titanium, and oxygen atoms deduced from their Wyckoff positions and the corresponding occupancies were 14, 16, and 53 atoms respectively. The chemical composition determined for this structure was \( \text{Bi}_{1.75} \text{Ti}_2 \text{O}_{6.62} \). It was experimentally confirmed that the non-stoichiometric pyrochlore phase is prevalent in \( \text{Bi}_{2-x} \text{Ti}_2 \text{O}_{7-1.5x} \) with \( x \sim 0.25 \) (rich in Ti).

Similarly, Figure 2.2. (B) shows the XRD patterns of \( \text{Bi}_{12} \text{TiO}_{20} \) and \( \text{Bi}_4 \text{Ti}_3 \text{O}_{12} \) powders that were synthesized using the co-precipitation method and the films deposited only on FTO. There was a limitation to deposit the sillenite structure on the silicon substrate due to the formation of \( \text{Bi}_{12} \text{SiO}_{20} \) impurity. The XRD patterns show that both structures are single phase. All peaks were indexed according to JCPDS No. 00-034-0097 and No. 00-035-0795 for \( \text{Bi}_{12} \text{TiO}_{20} \) and \( \text{Bi}_4 \text{Ti}_3 \text{O}_{12} \), respectively.

Based on the Rietveld refinement of the three structure, using the DFT/PBE computational method, the crystal structure of the nonstoichiometric \( \text{Bi}_{1.75} \text{Ti}_2 \text{O}_{6.62} \) structure systematically investigated compared to that of the ideal stoichiometric \( \text{Bi}_2 \text{Ti}_2 \text{O}_7 \) structure for comparison. The \( \text{Bi}_{12} \text{TiO}_{20} \) and \( \text{Bi}_4 \text{Ti}_3 \text{O}_{12} \) structures were also investigated. Figure 2.3. shows the most relevant relaxed structures for: the stoichiometric structure (a), non-stoichiometric structure (b), \( \text{Bi}_{12} \text{TiO}_{20} \) (c), and \( \text{Bi}_4 \text{Ti}_3 \text{O}_{12} \) (d). Table 2.2 reports their corresponding lattice parameters.
For the non-stoichiometric compound, the structure with the lowest energy was obtained for the configuration displaying a direct interaction between 2 Bi and 3 O vacancies (Figure 2.3, b). This interaction leads to the formation of a small cage in the lattice. Interestingly, upon relaxation, this structure retains very similar lattice parameters (lengths and angles) relative to the stoichiometric structure, in good agreement with the experimental data (Table 2.2.).

Table 2.2. Lattice parameters measured by the Rietveld refinement (Exp.) and calculated using DFT/PBE (DFT) of pyrochlore structure (Bi$_{1.75}$Ti$_2$O$_{6.62}$ and Bi$_2$Ti$_2$O$_7$), sillenite (Bi$_{12}$TiO$_{20}$), and perovskite-like Bi$_4$Ti$_3$O$_{12}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameters (Å, Degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td>Bi$_{1.75}$Ti$<em>2$O$</em>{6.62}$ (experimental)</td>
<td>10.350</td>
</tr>
<tr>
<td>Bi$_2$Ti$_2$O$_7$ (DFT)</td>
<td>10.328</td>
</tr>
<tr>
<td>Bi$_{1.75}$Ti$<em>2$O$</em>{6.62}$ (DFT)</td>
<td>10.290</td>
</tr>
<tr>
<td>(aggregated vacancies)</td>
<td></td>
</tr>
<tr>
<td>Bi$_{1.75}$Ti$<em>2$O$</em>{6.62}$ (DFT)</td>
<td>10.339</td>
</tr>
<tr>
<td>(separated vacancies)</td>
<td></td>
</tr>
<tr>
<td>Bi$<em>{12}$TiO$</em>{20}$ (experimental)</td>
<td>10.171</td>
</tr>
<tr>
<td>Bi$<em>{12}$TiO$</em>{20}$ (DFT)</td>
<td>10.142</td>
</tr>
<tr>
<td>Bi$_4$Ti$<em>3$O$</em>{12}$ (experimental)</td>
<td>5.407</td>
</tr>
</tbody>
</table>
By contrast, another non-stoichiometric structure displaying well-separated Bi and O vacancies was found to be 0.2 eV less stable than the previous one. In this case, the various atomic positions are strongly displaced upon relaxation from their initial positions, leading to different lattice parameters (especially the angles). The configuration with aggregated vacancies shows less cubic structure distortion ($\alpha, \beta, \gamma = 91, 90.2, 90.4^\circ$) in comparison with the configuration with well-separated vacancies ($\alpha, \beta, \gamma = 90.7, 88.8, 88.5^\circ$). Therefore, the structure with a small cage of defects was chosen for the following discussion of the computed material. The formation energy of the stoichiometric Bi$_2$Ti$_2$O$_7$ was calculated to be -1.608 eV per Bi atom, whereas that of Bi$_{1.75}$Ti$_2$O$_{6.62}$ was calculated to be -1.783 eV per Bi atom. This confirms that the nonstoichiometric structure is more stable, indicating that it is more favorable to obtain experimentally.
Figure 2.3. DFT-optimized lowest-energy structures obtained using the PBE functional for (a) perfect Bi$_2$Ti$_2$O$_7$, (b) defect-containing Bi$_{1.75}$Ti$_2$O$_{6.62}$ material with aggregated Bi and O vacancies, (c) Bi$_{12}$TiO$_{20}$, and (d) Bi$_4$Ti$_3$O$_{20}$. Color legend: Bi in purple, Ti in gray, O in red, and Bi (O) vacancies in dotted circles.

Bi$_{12}$TiO$_{20}$ was modeled as a cubic crystal structure in a sillenite family. Figure 2.3.c shows the most relaxed crystal structure of the Bi$_{12}$TiO$_{20}$. The adopted model contains 2 functional units (Bi$_{24}$Ti$_2$O$_{40}$) or 66 atoms. The least symmetrical phase of bismuth titanate is Bi$_4$Ti$_3$O$_{12}$ with a pseudo-orthorhombic crystal structure. Its model contains four functional units (Bi$_{16}$Ti$_{12}$O$_{48}$) with 76 atoms as shown in Figure 2.3. d. The sillenite structure has a cubic symmetry of the $I23$ space group. It has a general formula of Bi$_{12}$MO$_{20}$, where M is the tetravalent transition metal (Ti$^{4+}$) that forms the TiO$_4$ tetrahedra. The TiO$_4$ tetrahedra occupy the corners and the center of the cell lattice. The Bi–O
polyhedron network connects to the geometrically regular TiO₄ tetrahedra. Bismuth (Bi³⁺) is penta coordinated to three types of oxygen atoms forming a distorted polyhedra and a stereo chemically active 6 s² lone electron pair. Relaxation of the lattice parameter yields a = 10.142 Å, which is consistent with the measured value of a = 10.171 Å and previously reported values.⁴³⁴⁴ The Ti-O bond length is experimentally found to be 1.72 Å, and the five Bi-O bonds are bonds are 2.65, 2.62, 2.21, 2.19 and 2.07 Å with ± 0.01% error. A similar trend between measured and calculated values was obtained for the bond lengths was observed. The calculated single Ti-O bond length was 1.849 Å; the five Bi-O bond lengths were 2.59, 2.56, 2.25, 2.24, and 2.12 Å with ± 0.01% error.

The refined Bi₄Ti₃O₁₂ aurivillius (perovskite-like) structure is shown in Figure 2.3. (d). The model contains four functional units (Bi₁₆Ti₁₂O₄₈) with 76 atoms. It shows a pseudo-orthorhombic crystal structure in the Aba2 space group. The experimental lattice parameters shown in Table 2.2. are consistent with the calculated values and the literature.⁴⁵-⁴⁷ The Bi₄Ti₃O₁₂ structure is composed of fluorite bismuth-oxide (Bi₂O₂)²⁺ layers between perovskite-like (Bi₂Ti₃O₁₀)²⁻ layers along the c-axis, as shown in Figure 2.4. d. There are two types of Ti atoms, Ti (1) in the middle of the perovskite-like layer and Ti (2) at the connection between the perovskite-like and the bismuth-oxide layers, both of them octahedrally coordinated. The bond lengths from Rietveld refinement were 1.74, 1.96, and 2.20 Å for Ti (1) in the octahedral configuration. The second titanium, Ti (2), is in a distorted octahedra with Ti-O bond lengths of 1.72, 1.85, 2.10, and 2.27 Å. These values are notably consistent with those obtained from the most relaxed calculated values with 3 bond lengths: for Ti (1)-O: 1.87, 1.99 and 2.03 Å; for Ti (2)-O: 1.78, 1.91, 2.09, and 2.31 Å. The Bi atom in the Bi₂O₂²⁺ layer has three Bi-O bonds of lengths 2.32, 2.41, and
3.02 Å. Bi (2) in (Bi$_2$Ti$_3$O$_{10}$)$^{2-}$ has four different Bi-O bonds of 2.33, 2.41, 2.51, and 2.83 Å. Similar values were obtained from the relaxed structure with 2.34, 2.47, and 3.20 Å for Bi (1) and 2.23, 2.29, 2.39, and 2.86 Å for Bi (2). The good agreement between the experimental and theoretical parameters reflects the validity of the model adopted. The optoelectronic properties of these structures are then calculated.

### 2.2.2. Electronic structure

Figure 2.4 shows the electronic density of states (DOS) computed using the HSE06 functional for Bi$_{1.75}$Ti$_2$O$_{6.62}$, stoichiometric Bi$_2$Ti$_2$O$_7$, Bi$_{12}$TiO$_{20}$, and Bi$_4$Ti$_3$O$_{20}$. The energy dispersion curves of these materials computed using the PBE functional are given in Figure 2.5.

For the pyrochlore structure, the electronic analysis reveals that the valence-band states are governed by occupied O 2p orbitals with very weak contributions from Bi 6s orbitals, whereas the conduction-band states are predominantly composed of Ti 3d orbitals. Both compounds are direct (at the G or X point) semiconductors (Figure 2.5. a and b), with band gap energies of 3.7 eV for Bi$_2$Ti$_2$O$_7$ (Figure 2.4a) and 3.4 eV for Bi$_{1.75}$Ti$_2$O$_{6.62}$ (Figure 2.4b). The lowest-energy band gaps of these materials originate primarily from O 2p$^6$ – Ti 3d$^0$ orbital transitions.
Figure 2.4. Electronic DOSs obtained using the HSE06 functional for (a) stoichiometric Bi$_2$Ti$_2$O$_7$ and (b) non-stoichiometric Bi$_{1.75}$Ti$_2$O$_{6.62}$, (c) Bi$_{12}$TiO$_{20}$, (d) Bi$_4$Ti$_3$O$_{20}$ material in their most stable configurations, as reported in Fig. 2. Color legend: total DOS in black; DOSs projected onto Bi in red, onto Ti in blue, and onto O atoms in green. Potentials for valence band edge, conduction band edge, and flat band estimated from Mott–Schottky analysis are also represented on the RHE scale (pH 13.2) for the Bi$_{1.75}$Ti$_2$O$_{6.62}$.

By contrast, the DOSs calculated using the PBE functional yield much smaller band gap energies of 2.5 eV for Bi$_2$Ti$_2$O$_7$ and 2.3 eV for Bi$_{1.75}$Ti$_2$O$_{6.62}$, consistent with previous
theoretical studies of pyrochlore bismuth titanate.\textsuperscript{7, 48} The spin–orbit coupling effect was also performed on the electronic structures of Bi\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} and Bi\textsubscript{1.75}Ti\textsubscript{2}O\textsubscript{6.62} using the PBE functional, obtaining small decreases in the band gaps of 0.1 and 0.2 eV, respectively. By comparing these relative shifts to the values obtained using the HSE06 functional, the band gaps are predicted to be 3.6 eV for Bi\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} and 3.2 eV for Bi\textsubscript{1.75}Ti\textsubscript{2}O\textsubscript{6.62}, in very good agreement with the measured values.

The calculated electronic density of states (DOS) for the sillenite Bi\textsubscript{12}TiO\textsubscript{20} and perovskite-like Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} structures using the DFT/HSE06 method are shown in Figure 2.4.c and 2.4.d, respectively. Their calculated energy dispersion curves using the DFT/PBE method are provided in Figures 2.5. c and 2.5. d respectively. For Bi\textsubscript{12}TiO\textsubscript{20}, similar to the pyrochlore structure, the valence-band states in a wide energy range below the Fermi level are formed by occupied O 2p orbitals and weak contribution from Bi 6s orbitals, whereas the main difference is that the conduction-band states in the 1 eV range above the bottom part are mainly composed of empty Bi 6p orbitals (Figure 2.4. c). This results in narrowing the band gap compared to other two structure. The calculations predict a direct band gap (at the Γ or H point) semiconductor (Figure 2.5. c) with a band gap energy of 3.1 eV. The lowest-energy band gap of this material originates from the direct O 2p\textsuperscript{6} – Bi 6p\textsuperscript{0} orbital transitions. For Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12}, the electronic analysis reveals that valence-band states in a wide energy range below the Fermi level are dominated by O 2p orbitals with negligible contributions from Bi 6s orbitals, whereas the conduction-band states primarily consist of empty Ti 3d orbitals (Fig. 2.4. d). This material is predicted as an indirect (from T to X or Γ points) semiconductor (Figure 2.5. d) with a larger band gap of 3.6 eV, characterized by indirect transitions from O 2p\textsuperscript{6} to Ti 3d\textsuperscript{0} orbitals. Hence, it can be concluded that the
contribution of the Bi$^{3+}$ empty 6p orbitals to the conduction band resulted in narrowing the band gap. This is attributed to the with lower energy of Bi$^{3+}$ 6p orbitals in comparison to Ti$^{4+}$ 3d orbitals. The effect of bismuth is clearer in the bismuth-rich structure.

![Electronic band structure diagrams](image)

Figure 2.5. Electronic band structure diagrams along the high-symmetry k point obtained using the PBE functional for (a) stoichiometric Bi$_2$Ti$_2$O$_7$, (b) non-stoichiometric Bi$_{1.75}$Ti$_2$O$_{6.62}$, (c) Bi$_{1.5}$Ti$_2$O$_{20}$, (d) Bi$_4$Ti$_3$O$_{20}$; EF is set at 0 eV.

### 2.2.3. Exciton separation and Dielectric properties

The dielectric constant is an important parameter that represents the ability of a dielectric material to screen the external electric field by polarization. The dielectric constant is a
frequency-dependent parameter and consists of two components ($\varepsilon_r$): the electronic one ($\varepsilon_e$), which is linked to polarization from reorganization of the electronic density (optical), and the vibrational one ($\varepsilon_{vib}$), which involves ionic motion.

At high frequencies relevant to the UV-Vis region considered in the experimental study ($10^{14}$–$10^{15}$ Hz), the dielectric constant of the non-stoichiometric pyrochlore structure is deduced via spectroscopic ellipsometry contains only the electronic contribution. At lower frequencies ($10^{13}$ Hz), the vibrational contribution dominates. Through retro-simulation of the experimental data, the film thickness was deduced and the corresponding refractive index (n) and the absorption index (k) were calculated. (Figure 2.6.)

Figure 2.6. Refractive index components measure by spectroscopic ellipsometry for the Bi$_{1.75}$Ti$_2$O$_{6.62}$/Si film.

To correlate the complex refractive index with the dielectric properties, the following equation is applied:
\[ \varepsilon = \varepsilon_1 + i\varepsilon_2 = N^2 = (n + ik)^2 \]  

Thus, the dielectric constant can be deduced as follows:

\[ \varepsilon_1 = n^2 - k^2. \]  

Concerning the electronic contribution to the dielectric constant \((\varepsilon_\infty)\), Figure 2.7. displays the results measured via ellipsometry and calculated using the DFPT/HSE06 method through the real part \(\varepsilon_1(\omega)\) of the frequency dependent dielectric function (see Computational methods for more details).

![Graph](image)

Figure 2.7. The dielectric function for the Bi\(_{1.75}\)Ti\(_2\)O\(_{6.62}\) structure measured via spectroscopic ellipsometry (solid blue line) and those calculated using the HSE06 functional for the same non-stoichiometric structure (dashed blue line) and for the stoichiometric compound Bi\(_2\)Ti\(_2\)O\(_7\) (solid red line).

Experimentally, the electronic dielectric constant \(\varepsilon_\infty\) was found to be equal to 9.8 at a band gap of 3.3 eV. From the calculations, dielectric constants of 8.8 and 6.5 were obtained for
the stoichiometric Bi$_2$Ti$_2$O$_7$ compound and the nonstoichiometric Bi$_{1.75}$Ti$_2$O$_7$ compound, respectively. Moreover, both structures were found to be isotropic materials along the xx, yy and zz directions. This means that the light absorption and the subsequent exciton dissociation do not depend on the direction (x, y or z) of polarization of the light. In comparison with TiO$_2$ ($\varepsilon_\infty = 6$), the bismuth titanate structure possesses a higher dielectric constant.\textsuperscript{37} The ionic contributions $\varepsilon_{\text{vib}}$ were calculated using the DFPT/ PBE approach. For the stoichiometric Bi$_2$Ti$_2$O$_7$ compound a value of 80.1 was obtained in all three crystallographic directions. However, for the non-stoichiometric Bi$_{1.75}$Ti$_2$O$_7$ structure, the ionic contributions were 56.6, 76.8 and 87.4 in the xx, yy and zz directions, respectively. Higher dielectric constants were previously reported for these materials (101 and 104),\textsuperscript{49, 50} but those observed here still surpass the dielectric constant value of 45.7 for TiO$_2$.\textsuperscript{44}

Then the optical ($\varepsilon_\infty$) and macroscopic ($\varepsilon_r$) dielectric constant tensors of Bi$_{12}$TiO$_{20}$ and Bi$_4$Ti$_3$O$_{12}$ crystals were calculated using the PBE and HSE06 exchange-correlation functionals. Table 2.3 summarizes the obtained components in the three principle crystallographic directions. The real part of the dielectric function ($\varepsilon_1$) as a function of the incident radiation energy in the range of 0-8 eV is shown in Figure 2.8. Because of the cubic symmetry of sillenite, the dielectric tensor is isotropic with $\varepsilon_{xx}=\varepsilon_{yy}=\varepsilon_{zz}$. Both compounds have similar curvatures, although starting edges are dislocated because of different band gaps. Such similarities arise from the similarity in band structure and electrons transitions. The real part ($\varepsilon_1$) describes the electronic part ($\varepsilon_\infty$) of the dielectric constant of the materials at the band gap energy.
Figure 2.8. Real part of the frequency-dependent dielectric function along three principal light polarization vectors of (a) Bi12TiO20 and (b) Bi4Ti3O12 structures, which were obtained using HSE06.

The electronic part of the dielectric constant tensor was deduced from $\varepsilon_1$ computed using HSE06 as shown in Figure 2.8., while the ionic component tensors for both components were computed using PBE functional following the methodology described in Computational Methods. For sillenite, a high dielectric constant $\varepsilon_r$ of 31.2 was found along the three principal directions with $\varepsilon_\infty = 6.26$ (Figure 2.8. a) and $\varepsilon_{\text{vib}} = 25.0$ as shown in Table 2.3. the calculated macroscopic dielectric constant is consistent with the reported experimental one of 41 using the dielectric resonator technique.\(^{44, 51}\) The perovskite-like structure retains higher macroscopic dielectric constant than sillenite,\(^{52}\) with values of 56.8, 67.3 and 47.4 along the $xx$, $yy$, $zz$ directions, respectively, and 57.2 as an average value. This may be explained by the layered structure that favors the charge separation. The
vibrational component values are 51.9, 62.1 and 40.4 along the principle directions. The average electronic contribution is 5.72 deduced from the $xx$, $yy$, and $zz$ direction values interpreted from Figure 2.8. The dielectric constant of the perovskite-like structure is reported to be temperature-dependent and increases with increasing temperature. At the relaxing frequency, the major contribution of the total dielectric constant in both crystals comes from the ionic part because of the high electronegativity of oxygen. The ionic contribution is proportional to the oxide (TiO) large Born effective charges and inversely proportional to the photon frequency. At very high frequencies (>10$^{12}$ Hz) the ionic contribution tends to decrease because the ions respond more slowly than the electrons to an applied field, which results in a larger contribution from the electronic part. A dielectric constant tensor can also help characterizing optically active materials when small non-diagonal components appear, even if the crystal structure is cubic.

Table 2.3. Optical ($\varepsilon_\infty$), vibrational ($\varepsilon_{\text{vib}}$) and macroscopic ($\varepsilon_r$) dielectric constant components in three principal directions of Bi$_{1.75}$Ti$_2$O$_{6.62}$, Bi$_2$Ti$_2$O$_7$, Bi$_{12}$TiO$_{20}$ and Bi$_4$Ti$_3$O$_{12}$ structures obtained using PBE for ($\varepsilon_{\text{vib}}$) and HSE06 for ($\varepsilon_\infty$), respectively.
<table>
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<th>Direction</th>
<th>ε_e</th>
<th>ε_vib</th>
<th>ε_r</th>
</tr>
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<td>xx</td>
<td>56.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi_{1.75}Ti_{2}O_{6.62} yy</td>
<td>6.5</td>
<td>76.8</td>
<td>93.1</td>
</tr>
<tr>
<td>zz</td>
<td>87.4</td>
<td></td>
<td></td>
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<tr>
<td>Bi_{2}Ti_{2}O_{7} xx=yy=zz</td>
<td>8.8</td>
<td>80.1</td>
<td>88.9</td>
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<tr>
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<td>6.26</td>
<td>25.0</td>
<td>31.2</td>
</tr>
<tr>
<td>Bi_{2}Ti_{3}O_{12} yy</td>
<td>5.29</td>
<td>62.1</td>
<td>67.3</td>
</tr>
<tr>
<td>zz</td>
<td>7.00</td>
<td>40.4</td>
<td>47.4</td>
</tr>
<tr>
<td>TiO_{2}</td>
<td>average</td>
<td>6</td>
<td>39.7</td>
</tr>
</tbody>
</table>

Interestingly, these compounds show high dielectric constants which is comparable to TiO₂ for the case of sillenite and perovskite structures and even higher than TiO₂ for the pyrochlore structure.

### 2.2.4. Absorption properties

In Figure 2.9. a, the measured and calculated absorption coefficients of non-stoichiometric Bi_{1.75}Ti_{2}O_{6.62} are plotted, together with the corresponding results calculated for stoichiometric Bi_{2}Ti_{2}O_{7}. The experimental value of the absorption coefficient was deduced from the imaginary part of the dielectric constant measured via spectroscopic ellipsometry. The band gap of the non-stoichiometric Bi_{1.75}Ti_{2}O_{6.62} structure was measured using
spectroscopic ellipsometry. The inset of Figure 6 shows the Tauc plot for the direct transition,$^{56}$ indicating a band gap of approximately 3.3 eV.

Figure 2.9. (a) Absorption coefficients of the spectra of Bi$_{1.75}$Ti$_2$O$_{6.62}$ obtained via ellipsometric spectroscopy (solid blue line) and computed using the HSE06 functional, together with the results computed for Bi$_2$Ti$_2$O$_{6.62}$. The inset shows the Tauc plot of the measured results for Bi$_{1.75}$Ti$_2$O$_{6.62}$. (b) The Optical absorption coefficient spectra of Bi$_{12}$TiO$_{20}$ and Bi$_4$Ti$_3$O$_{12}$ structures, which were obtained using HSE06.

It can be seen that the calculated absorption coefficient for Bi$_{1.75}$Ti$_2$O$_{6.62}$ (dashed blue line) agrees well with the measured one. Both show an onset of absorbance at approximately 3.3 eV, consistent with the observed band gap energy. It can be seen that the non-
stoichiometric structure exhibits a narrowing of the band gap with respect to the stoichiometric Bi$_2$Ti$_2$O$_7$ structure. This confirms that an accurate description of the absorption properties of the pyrochlore bismuth titanate structure is achievable by considering non-stoichiometric effects, i.e., the presence of (Bi,O) vacancies in the structure.

The band gap values previously reported in the literature are much smaller: theoretically, they have been reported to be 2.63 and 2.89 eV$^{48}$ and experimentally, they have been found to be 2.9,$^{57}$ 2.95,$^{8}$ and 3.0 eV.$^{9}$ These lower previously reported band gaps can be explained by the presence of secondary phases (e.g., Bi$_4$Ti$_3$O$_{12}$) with smaller band gaps. A reduced band gap was indeed observed for the sample that contained a Bi$_4$Ti$_3$O$_{12}$ phase ($\sim$ 2.95 eV) with a Ti/Bi ratio of 1, as shown in Figure 2.10. The purity of the sample is crucial to determine its intrinsic band gap. It has been reported that as the fraction of the Bi$_4$Ti$_3$O$_{12}$ phase in the sample increases, the color of the powder changes from pale white to yellow.$^{33}$ Hence, accurate measurements of the band gap can only be achieved using the single phase material.
The absorption properties of the sillenite and perovskite-like structures were determined from the powder using DR.UV-Vis spectra. Figure 2.11. a shows the diffuse reflectance UV-Vis spectra of Bi$_{12}$TiO$_{20}$ and Bi$_4$Ti$_3$O$_{12}$ powders. The spectrum of the Bi$_4$Ti$_3$O$_{12}$ material shows an absorption edge at 380 nm. In contrast, the absorption edge of Bi$_{12}$TiO$_{20}$ is shifted to the visible region probably because of defects in the structure. Tauc plots corresponding to the obtained spectra (Figure 2.10. b) show measured band gaps of 3.0 and 3.3 eV for Bi$_{12}$TiO$_{20}$ and Bi$_4$Ti$_3$O$_{12}$, respectively. The calculated optical absorption coefficient spectra, presented in Figure 2.9. b were obtained by averaging the imaginary and real parts of the dielectric function, computed using HSE06 over three polarization vectors as a function of the wavelength of the incident light. A slight blue shift is observed in the absorption coefficient of calculated data. Generally, the Kubelka-Munk function
shows this red shift in the absorption edge in comparison with the absorption coefficient. The absorption coefficient is more accurate to investigate the absorption properties as described in the chapter 1. Both compounds exhibit low absorbance in the visible-light range. For the perovskite-like structure, the principal absorption edge is located at 340 nm, which mainly originates from the electronic transitions from O 2p- to Bi 6p- states. This result obviously shows that the bismuth titanate sillenite structure is a better photon absorber than the perovskite-like one.

Figure 2.11. (a) Diffuse reflectance UV-Vis spectra of Bi$_{12}$TiO$_{20}$ and Bi$_4$Ti$_3$O$_{12}$ powders and their corresponding Tauc plots (b).

Detailed investigation for Bi$_{12}$TiO$_{20}$ structure was carried out to identify the crucial effects of the Bi/Ti stoichiometry on the absorption edge and to explain the red shift. The stoichiometry of the compounds was confirmed by combining ICP result and the Rietveld analysis.
Figure 2.12. (a) The XRD patterns of the sillenite structure with different Bi/Ti ratio 4.7:1, 12:1, and 14:1 and their corresponding DR.UV-Vis spectra (b).

absorption edge of the sample with Bi/Ti ratio of 4.7 shows a blue shift in comparison to the sample with 12:1, whereas the sample with excess bismuth of Bi: Ti = 14:1 shows a red shift. These results confirm that, although the XRD patterns appear identical, non-stoichiometry of the structure causes varied information of the band edges. This explains the inconsistency of the previously reported experimental studies. The sillenite structure is indeed UV responsive material and the smaller band gaps (2.4 eV, 17 2.78 eV, 58 2.75 eV, 16 2.94 eV, 59 3.1 eV, 60 and 3.2 eV 61 are not reflecting the single phase material.

2.2.5. Charge carrier transport properties

The effective mass of holes and electrons is an excellent descriptor of the charge carrier transport properties of the crystal. They are related to the curvature of the valence band (for the holes) or conduction band (for the electrons) around the extremum of the band. The determination of the charge carrier effective masses along different crystallographic
directions provides access to the possible anisotropy of charge carriers through the crystal structure of the material. As experimentally demonstrated, the effective mass of both, holes and electrons should be smaller than $0.5m_0$ at least in one crystallographic direction to obtain good charge carrier transport properties.$^{62-64}$

The effective mass tensors of photo generated holes ($m_h^*$) and electrons ($m_e^*$) were computed at the band edges of Bi$_2$Ti$_2$O$_7$ and Bi$_{1.75}$Ti$_2$O$_6.62$, Bi$_{12}$TiO$_{20}$, and Bi$_4$Ti$_3$O$_{12}$ to evaluate their charge-carrier transport properties. Table 2.4 reports the values calculated in the three principal crystallographic directions. For Bi$_2$Ti$_2$O$_7$, the effective electron and hole masses were found to be relatively small (0.17, 0.2, and 0.87 for electrons and 0.56, 0.75, and 3.5 for holes in the [001], [010], and [100] directions, respectively). In the case of Bi$_{1.75}$Ti$_2$O$_6.62$, the effective masses were found to be slightly higher both for electrons (0.3, 0.39, and 1.66, respectively) and for holes (0.45, 36.4, and 14, respectively). The increased carrier effective masses in the non-stoichiometric structure is explained by the presence of defects which act as recombination centers for the carriers.

Interestingly, the sillenite structure showed the smallest electron and hole effective mass was found along the $zz$ direction with a value of 0.05 $m_0$ (units of the electron mass). This result guarantees notably high hole and electron mobility and good charge carrier transport properties because it is less than $0.5m_0$. However, the migration of the electron and hole in identical directions may result in a poor charge separation at the surface of the material. For efficient separation, the charges must travel in two different crystallographic directions. Still it is important to note that the sillenite structure have a very good hole transport properties which may be attributed to the increased hybridization of the bismuth in the valence band. The bismuth titanate perovskite-like structure has high electron mobility.
(0.14 \( m_0 \)) in the \( xx \) and \( zz \) directions and higher hole mobility by one order of magnitude (0.014 \( m_0 \)) in the \( zz \) direction. The notably small hole and electron effective masses in two different directions prove that charge carriers in the perovskite-like structure are separated by a single-phase material, known as the bulk photovoltaic effect, which is interesting for ferroelectric properties. Generally, because of the high electronic carrier mobility, these compounds may act as promising electronic materials.

Table 2.4. Effective masses of holes \( (m_h^*/m_0) \) and electrons \( (m_e^*/m_0) \) in three principal directions of \( \text{Bi}_2\text{Ti}_2\text{O}_7 \), \( \text{Bi}_{1.75}\text{Ti}_2\text{O}_{6.62} \), \( \text{Bi}_{12}\text{TiO}_{20} \) and \( \text{Bi}_4\text{Ti}_3\text{O}_{12} \) structures, which were obtained using the DFT/PBE method. \( m_0 \) is the free electron mass.

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<th>Effective masses</th>
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<th>( m_e^* )</th>
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<td>100 010 001</td>
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<td>( \text{Bi}_2\text{Ti}_2\text{O}_7 )</td>
<td>3.5 0.75 0.56</td>
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<td>( \text{Bi}_{1.75}\text{Ti}<em>2\text{O}</em>{6.62} )</td>
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<td>1.66 0.39 0.3</td>
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<tr>
<td>( \text{Bi}<em>{12}\text{TiO}</em>{20} )</td>
<td>0.52 0.09 0.05</td>
<td>1.27 0.14 0.05</td>
</tr>
<tr>
<td>( \text{Bi}_4\text{Ti}<em>3\text{O}</em>{12} )</td>
<td>0.14 0.94 0.14</td>
<td>0.16 0.74 0.01</td>
</tr>
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</table>
2.2.6. Band edge positions

To determine the flat band potential, Mott–Schottky measurements of the Bi$_{1.75}$Ti$_2$O$_{6.62}$, Bi$_{12}$TiO$_{20}$, and Bi$_4$Ti$_3$O$_{12}$ were performed using the film on the FTO substrate. A frequency range of 70 to 150 Hz was chosen by analyzing the Bode plot (Figure 2.13. a), and the potential range (0.6–1.0 V vs. RHE) was chosen to be the double-layer region in which there is no faradic current (Figure 2.13. b).
Figure 2.13 (a) Bode plot and (b) Cyclic voltammetry Bi$_{1.75}$Ti$_2$O$_{6.62}$/FTO film measured in 0.1 M NaOH solution, pH 13
Figure 2.14 shows the Mott–Schottky plot for the Bi$_{1.75}$Ti$_2$O$_{6.62}$ Bi$_{12}$TiO$_{20}$, and Bi$_4$Ti$_3$O$_{12}$ films on FTO. It can be seen from the positive slope of all the structures that these material has an n-type nature.

![Image of Mott-Schottky plots]

Figure 2.14. Mott-Schottky plots of pyrochlore, sillenite, and perovskite-like structures and their schematic band positions with respect to TiO$_2$.

According to the Mott–Schottky equation:

$$\frac{1}{C^2} = \frac{2}{eA^2 \varepsilon \varepsilon_0 N_D} (E_{app} - E_F - \frac{k_B T}{e})$$  \hspace{1cm} (2.3)
where \( C \) is the capacitance, \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon_r \) is the dielectric constant, \( N_D \) is the majority carrier concentration, \( A \) is the electrode area, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( e \) is the elementary charge. The value of the dielectric constant \( \varepsilon_r \) (73.6) was obtained from theoretical calculations of both the ionic and electronic vibrational contributions because the Mott–Schottky measurement was performed at relatively low frequencies and therefore included the ionic vibrational contribution. The flat band potential \( E_{FB} \) was deduced from the intercept of the plot as a function of the applied potential \( E \), yielding an \( E_{FB} \) of \(-0.12 \text{ V vs. RHE.} \) The majority carrier concentration \( (N_D) \) was found to be \( 3.26 \times 10^{18} \text{ cm}^{-3} \) from the slope of the plot. Next, the density of states in the conduction band \( (N_C) \) was calculated using eqn (2.4):

\[
N_C = \left( \frac{2}{h^3} \right) (2\pi m^*_e kT)^3
\]

(2.4)

where \( h \) is Planck’s constant and \( m^*_e \) is the effective electron mass. From this measurement, the electron effective mass was found to be \( 0.3m_0 \). The difference between the bottom of the conduction band \( (E_C) \) and \( E_{FB} \) was deduced using eqn (2.5):

\[
E_C - E_{FB} = -kT \ln \left( \frac{N_D}{N_C} \right)
\]

(2.5)

The edge of the conduction band was measured to lie at \(-0.47 \text{ V vs. RHE.} \) Consequently, \( \text{Bi}_{1.75}\text{Ti}_2\text{O}_{6.62} \) has a more negative conduction band edge than does \( \text{TiO}_2 \), whose conduction band edge has been reported to lie at \(-0.19 \text{ V vs. RHE under similar pH} \).
The result is added into Figure 3 on the RHE scale (pH 13.2). The parameters obtained through Mott–Schottky analysis are summarized in Table 2.5.

Table 2.5. Summary of the semiconductor properties of the pyrochlore structure deduced through Mott-Schottky analysis

<table>
<thead>
<tr>
<th>parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{\infty}$</td>
<td>10</td>
</tr>
<tr>
<td>$\varepsilon_{vib}$ (DFPT/PBE)</td>
<td>73.6</td>
</tr>
<tr>
<td>$N_D$</td>
<td>$3.26 \times 10^{18}$ cm$^{-3}$</td>
</tr>
<tr>
<td>$N_C$</td>
<td>$4.12 \times 10^{18}$ cm$^{-3}$</td>
</tr>
<tr>
<td>$m^*_e$</td>
<td>0.3</td>
</tr>
<tr>
<td>$E_c$</td>
<td>-0.47 V</td>
</tr>
<tr>
<td>$E_{FB}$</td>
<td>-0.12 V vs. RHE</td>
</tr>
</tbody>
</table>

All these structures showed more negatively located conduction band may allow this material to be applied as an alternative anode material in place of TiO$_2$ in dye-sensitized solar cells to increase the open-circuit potential.

To summarize the comparison with the well-studied material TiO$_2$, the most prominent difference was evident in the flat band potentials; Bi$_{1.75}$Ti$_2$O$_{6.62}$ possesses a more negatively located conduction band, although the band gap and absorption properties are
similar. To take full advantage of these properties, a Bi$_{1.75}$Ti$_{2}$O$_{6.62}$/TiO$_2$ composite may result in better overall performance than either TiO$_2$ or Bi$_2$Ti$_2$O$_7$ alone for photocatalytic reactions.\(^{66}\)

2.3. Experimental and theoretical methods

2.3.1. Chemicals

The following chemicals were used: bismuth nitrate pentahydrate (Aldrich, 99.999%), titanium iso-propoxide (Aldrich, 99.999%), glacial acetic acid (Fisher Scientific, 99.8%), ammonium hydroxide (Fisher Scientific, 29.44%), methoxy ethanol (Sigma, 99%), acetyl acetone (Aldrich, 99%), and sodium hydroxide (Sigma-Aldrich, 99.99%).

2.3.2. Synthesis of bismuth titanate powders and films

Bismuth titanate powders were synthesized using the co-precipitation method.\(^{33}\) Bi(NO$_3$)$_3$.5H$_2$O (10 mmol) was dissolved in 25 ml of glacial acetic acid under stirring at room temperature for 3 h until the solution became clear. Then, titanium isopropoxide was added to adjust the starting Ti/Bi molar ratio to values of 1, 1.23, 1.50, 1.75 and 2 for the pyrochlore structure and Ti/Bi=12 and 0.75 for sillenite and perovskite-like structures, respectively to form crystalline samples.

After 5 min of stirring, 33 ml of cold ammonium hydroxide was slowly added. When the pH became ~7, a white precipitate was formed, which was filtered and washed extensively with Milli-Q water (~18MΩ). After drying at 90 °C for 24 h, the obtained mixture was ground and heat treated at 550 °C, 600 °C, and 700 °C for 16 h in a static furnace for the
pyrochlore, sillonite, and perovskite-like structures, respectively. Bismuth titanate films were deposited using the chemical solution deposition method via the spin-coating technique. The starting solution was prepared by dissolving 3 mmol of Bi(NO$_3$)$_3$.5H$_2$O in 5 ml of glacial acetic acid. Methoxy ethanol (2.5 ml) was added to adjust the tension of the solution. Then, a stoichiometric amount of titanium isopropoxide (3.7 mmol, Ti/Bi molar ratio = 1.23, 0.75, 1/12) was added, causing the solution to turn light yellow. Acetyl acetone (1.5 ml) was added to prevent titanium complexation. In each cycle, the solution was spin coated onto a Si wafer or a fluorine-doped tin oxide (FTO) substrate at 3000 rpm for 30 s. Unless otherwise stated, the deposition was repeated over 10 cycles. Then, the film was dried for 5 min at 200 °C. Finally, it was calcined at 550 °C, 600 °C, and 700 °C for 2 h for the pyrochlore, sillonite, and perovskite, respectively.

2.3.3. Structural and optical characterization

X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advanced A25 diffractometer equipped with a Cu X-ray tube (Cu-K$_\alpha$; l = 0.15418 nm) operated at 40 kV and 40 mA in the Bragg–Brentano geometry using a linear position-sensitive detector with an opening of 2.9°. The diffractometer was configured with a 0.44° divergence slit, a 2.9° anti-scatter slit, 2.5° Soller slits, and a nickel filter to attenuate contributions from Cu-K$_\beta$ fluorescence. The XRD data were analyzed via the Rietveld method using the fundamental parameters approach, as implemented in the software TOPAS V4.2 (Bruker-AXS). The XRD pattern of pyrochlore bismuth titanate was refined using the cubic structure (space group Fd3m) taken from card 01-089- 4732 in the ICSD database. The profile parameters included the scale factor, a sample displacement parameter, and a three term polynomial
for the background. The fundamental parameters approach involves analytically calculating the instrumental broadening in the peak profile. The particle size was calculated from the Lorentzian contribution to this profile. The values of $R_{wp}$, $R_{Bragg}$, and the goodness of fit (GOF) were approximately 9, 3, and 2, respectively, for all refinements. Inductively coupled plasma (ICP) measurements were performed using an Agilent 720 Series ICP-OES instrument (Agilent Technologies). Digestion of the material was performed in an ETHOS 1 microwave digestion system (Milestone Srl). The thicknesses and complex refractive indexes ($n + ik$) of the films were determined by applying the spectroscopic ellipsometry technique to films deposited on Si substrates. Measurements were made via scanning in the 1-6 eV range using a Jobin-Yvon ellipsometer (UVISEL).

2.3.4. Electrochemical measurements

Electrochemical measurements were performed using Milli-Q water. Sodium hydroxide was used as received to prepare the required 0.1 M electrolyte with pH 13.2. All experiments were performed using a research-grade multi-channel potentiostat (VMP3, BioLogic Science Instruments). Cyclic voltammetry (CV) experiments were performed using a regular one-compartment electrochemical cell with a three-electrode configuration. A Pt wire and an Ag/AgCl (saturated KCl) electrode were used as counter and reference electrodes, respectively. All experiments were recorded against this reference electrode, which was reported on the reversible hydrogen electrode (RHE) scale pyrochlore bismuth titanate films on FTO were used as the working electrodes. The CV results were recorded at a scan rate of 10 mV.s$^{-1}$. Electrochemical impedance spectroscopy was performed to estimate the flat band potential of the prepared samples. Prior to impedance spectroscopy,
CV was conducted under Ar bubbling at a 10 mV.s\(^{-1}\) scan rate from a potential of 0 to 1.7 V vs. RHE to determine the potential window for Mott–Schottky analysis. For this analysis, a potential range of 0.5–1 V vs. RHE was chosen, in which the faradic current remains negligible. Impedance spectra were recorded between 10 Hz and 200 kHz, and the amplitude of the superimposed sinusoidal potential signal was 5 mV for each of the 70 steps.

2.3.5. Computational methods

Starting from the cubic crystal structure of Bi\(_2\)Ti\(_2\)O\(_7\) (pyrochlore phase; space group is Fd3m), which contains 16 functional units (Bi\(_{16}\)Ti\(_{16}\)O\(_{56}\)) or 88 atoms (see Figure 2.3. a), the non-stoichiometric Bi\(_{1.75}\)Ti\(_2\)O\(_{6.62}\) structures were modeled by removing two neutral Bi atoms and three neutral O atoms from various possible sites in the cell to obtain Bi\(_{1.75}\)Ti\(_2\)O\(_{6.625}\). Several geometrical configurations were explored by paying particular attention to key structures exhibiting separated or aggregated Bi and O vacancies (Figure 2.15.).
Figure 2.15. DFT optimized-lowest energy structure for the Bi$_{1.75}$Ti$_2$O$_{6.62}$ material with Bi and O separated vacancies.

In the structural models, the oxidation states of the examined elements were Bi$^{3+}$, Ti$^{4+}$, and O$^{2-}$. The various generated structures were optimized using periodic DFT, as implemented in VASP$^{67}$ using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional$^{68}$ and the projected augmented plane wave (PAW) approach.$^{69}$ The configurations of the valence electrons adopted in the PAW potentials were 6s$^2$ 6p$^3$ for Bi, 3d$^3$ 4s$^1$ for Ti, and 2s$^2$ 2p$^4$ for O. Cutoff energies of 500 and 610 eV were used for the wave functions and charge augmentations, respectively. The convergence criterion for the SCF cycles was set to $10^{-5}$ eV per cell. The atomic coordinates and cell parameters were fully relaxed until all components of the residual forces reached values below 0.01 eV Å$^{-1}$. In all cases, the Brillouin zone was sampled using a 5 x 5 x 5 Monkhorst–Pack k-point grid.$^{70}$

For density-of-states (DOS) calculations, the screened Coulomb hybrid Heyd–Scuseria–Ernzerhof (HSE06) exchange–correlation functional,$^{71-73}$ was employed as implemented in
VASP,67,74-76 based on the optimized geometries obtained at the PBE level. The tetrahedron method with Blöchl corrections was used for the Brillouin-zone integration. As reported in ref. 30–32, the well-known limitation of GGA functionals (underestimated band gaps) is expected to be considerably mitigated through the use of HSE06.74

To calculate the UV-Vis optical absorption properties of these materials, the DFPT was applied as implemented in VASP using the HSE06 formalism. The optical properties were obtained from the frequency-dependent complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega)$ following a methodology described in the literature.73 The real part $\varepsilon_1(\omega)$ was obtained using the Kramers–Kronig relation and it is defined as the electronic contribution to the dielectric constant, whereas the imaginary part $\varepsilon_2(\omega)$ was calculated by summing all possible transitions from occupied to unoccupied states in the Brillouin zone weighted with the matrix elements describing the probabilities of transition. To determine the fraction of the light absorbed in these materials, the optical absorption coefficient $\alpha(\omega)$ (in cm$^{-1}$) was calculated for each compound as a function of the wavelength of the incident light using the following equations:

$$\alpha(\omega) = \frac{4\pi k(\omega)}{\lambda} \quad (2.5)$$

$$k(\omega) = \left(\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1}{2}\right)^{1/2} \quad (2.6)$$

where $\lambda$ and $\omega$ are the wavelength and frequency of the incident light, respectively, and $k(\omega)$ is the extinction coefficient or the imaginary part of the complex refractive index. The
vibrational contribution to the dielectric constant tensors ($\varepsilon_{\text{vib}}$) was obtained by computing
the full phonon spectrum of the crystal using DFPT and the PBE functional in the
framework of the linear response method implemented in VASP. The effective mass
tensors of photo generated holes ($m_h^*$) and electrons ($m_e^*$) at the band edges of these
compounds were computed based on their k-space band structures obtained from the PBE
functional using the following expression:

$$
\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 E_n(k)}{\partial k_i \partial k_j} \quad (i, j = x, y, z)
$$

(2.7)

Where $i$ and $j$ denote reciprocal components and $E_n(k)$ is the dispersion relation for the $n$-band. Note that the derivatives were evaluated numerically using the finite difference
method.
2.4. Summary

A study combining experimental and theoretical methods was conducted to investigate the optoelectronic properties of a series of bismuth titanates.

A clear distinction was made between the non-stoichiometric Bi$_{2-x}$Ti$_2$O$_{7-1.5x}$ structure ($x = 0.25$), and the ideal perfect stoichiometric configuration ($x = 0$) was observed. The calculated results for the band gap and absorption coefficient of the nonstoichiometric structure (Bi$_{1.75}$Ti$_2$O$_{6.62}$) exhibited excellent agreement with the band gap of 3.3 eV measured via ellipsometry, which is narrower than the band gap computed for the stoichiometric Bi$_2$Ti$_2$O$_7$ material (3.6 eV). The nature of the band gap was found to be direct as a result of a transition at the G or X point. Similarly, the compounds (Bi$_{12}$TiO$_{20}$ and Bi$_4$Ti$_3$O$_{12}$) have been synthesized and characterized with a synergic experimental and computational approach. Using the accurate HSE06 functional and taking spin-orbit coupling effect into account, both compounds exhibit relatively large optical band gaps 3.1 eV for sillenite and 3.6 eV for perovskite-like structures, respectively.

The calculated static dielectric constants exhibited high values of up to 80.1 for Bi$_{1.75}$Ti$_2$O$_{6.62}$, 31.2 for the sillenite structure, and an average of 57.16 for the perovskite-like structure. These results indicate excellent charge separation properties exceeding that of the TiO$_2$. The pyrochlore structure was found to be highly anisotropic, with high effective electron and hole masses in certain directions, which may result in lower charge carrier mobility. However, low electron and hole effective masses were observed for the sillenite and perovskite structure.
The flat band potentials were measured in 0.1 M NaOH solution (pH 13.2) for the three structures and was found to be -0.12, -0.1, and -0.2 vs. RHE for the non-stoichiometric pyrochlore, sillenite, and perovskite-like structures respectively. All were found more negative than those of the well-known TiO$_2$ compound. This study identified several key parameters of a series of bismuth titanates, which may have various potential applications, e.g., may be substituted for or mixed with TiO$_2$ is dye-sensitized solar cells and photocatalytic applications.

2.5. References

CHAPTER 3

Flux-assisted synthesis of SnNb$_2$O$_6$ for tuning photocatalytic properties$^2$

A flux-assisted method was used to synthesize SnNb$_2$O$_6$ as a visible-light-responsive metal oxide photocatalyst. The role of flux was investigated in detail using different flux to reactant molar ratios (1:1, 3:1, 6:1, 10:1, and 14:1) and different reaction temperatures (300, 500, and 600 °C). The obtained products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), diffuse reflectance UV-Vis spectroscopy, X-ray photoelectron spectroscopy (XPS), the Brunauer–Emmett–Teller method (BET), and high resolution scanning transmission electron microscopy (HRTEM). Flux-assisted synthesis led to tin niobate particles of platelet morphology with smooth surfaces. The synthesized crystal showed a 2D anisotropic growth along the (600) plane as the flux ratio increased. The particles synthesized with a high reactant to flux ratio (1:10 or higher) exhibited slightly improved photocatalytic activity for hydrogen evolution from an aqueous methanol solution under visible radiation ($\lambda > 420$ nm). The photo-deposition of platinum and PbO$_2$ was examined to gain a better understanding of electrons and hole migration pathways in these layered materials. The HR-STEM observation revealed that no preferential deposition of these nanoparticles was observed depending on the surface facets of SnNb$_2$O$_6$.

$^2$ This chapter was adapted from D. Noureldine, D. H. Anjum, K. Takanabe, Phys. Chem. Chem. Phys., 2014, 16, 10762-10769
3.1. Introduction

Energy demand has been increasing continuously in recent decades, and the world’s energy consumption is expected to double by the year 2050. This challenge has oriented scientific interest towards renewable energy sources that can both fulfill the global needs and address the environmental problems and the risk of oil depletion. Overall water splitting using photocatalysis has been introduced as a very promising method for future energy needs. It produces a clean, renewable, and high-density energy carrier, i.e., hydrogen. Numerous metal oxide photocatalysts have been reported to split water with high efficiency under UV irradiation. However, to efficiently utilize sunlight, absorption in the visible region should be utilized for photocatalysis. One promising approach is to combine d⁰ transition metals with metals that have s² d¹⁰ electron configurations, such as Sn²⁺. The hybridization between O 2p and metal s² orbitals results in a more strongly negative potential of the valence band than in oxides with only an O 2p contribution, thus minimizing the band gap. SnNb₂O₆ is a promising visible-light-responsive photocatalyst with a band gap of 2.3 eV. It has been reported to evolve either hydrogen or oxygen using sacrificial agents, suggesting that the band positions are suitable to achieve overall water splitting. The drawback of Sn²⁺ mixed metal oxide synthesis is that it suffers from the disproportionation of Sn²⁺ to Sn⁴⁺ and metallic Sn at high temperatures, which minimizes its activity when prepared by solid-state synthesis. The required high temperature for the synthesis does not offer control over the surface properties of photocatalytic materials, such as size, morphology and roughness. It is well known that the surface is a crucial part of the photocatalyst, where both the oxidation of water and the reduction of protons take place. Therefore, new synthetic routes are required to allow better control of characteristics in
final products.\textsuperscript{18} For the synthesis of SnNb\textsubscript{2}O\textsubscript{6} materials, hydrothermal methods\textsuperscript{19,20} and microwave-assisted synthesis\textsuperscript{21} have been used for dye degradation applications. The obtained products showed a visible response, but their synthesis method led only to low crystallinity.\textsuperscript{19,21} Recently, SnNb\textsubscript{2}O\textsubscript{6} synthesized by a hydrothermal method showed hydrogen evolution activity under visible light irradiation.\textsuperscript{20} The sample obtained by this method showed low crystallinity, but subsequent treatment at 800 °C was found to be effective in increasing the crystallinity. The flux-assisted synthesis is practical because it enhances the level of control over the sizes, surfaces and morphologies of photocatalytic metal-oxide solids\textsuperscript{18} achieved by dissolving the precursors in a eutectic salt that induces rapid diffusion and therefore the formation of products in shortened reaction times and at lower temperatures.\textsuperscript{18} The usage of lower temperatures and shorter reaction times compared to solid-state synthesis save energy and reduce the cost, which are highly attractive in comparison with a solid-state method.\textsuperscript{15,16} More interestingly, the flux-assisted method leads to the unique preferential growth of a specific facet that generally has lower interfacial energy than the other facets, which results in special morphologies, such as sheets, plates and flower-like shapes, that may have a beneficial effect on the photocatalytic activity of the material.\textsuperscript{22,23} Furthermore, this method leads to high crystallinity and non-defective materials via a recrystallization process that occurs while cooling down at certain temperatures. Controlling the rate of cooling greatly affects the final product.\textsuperscript{24} While cooling, the product particles nucleate homogenously in the liquid phase, and the rate of cooling defines the number of nuclei and the size of the product crystals.\textsuperscript{25} Kudo and coworkers reported the flux-assisted synthesis of SnNb\textsubscript{2}O\textsubscript{6} starting from a Sr\textsubscript{2}Nb\textsubscript{2}O\textsubscript{7} perovskite structure with SnCl\textsubscript{2} as a molten salt.\textsuperscript{26} The synthesis proceeds through an ion
exchange mechanism where Sn$^{2+}$ replaces the Sr$^{2+}$, resulting in a layered structure. However, they required a long reaction time (30 h), and the process of removing the excess SnCl$_2$ was quite difficult. They also reported the molten salt treatment of NaNbO$_3$ nanorods and Nb$_2$O$_5$ nanowires with SnCl$_2$, and the activity for hydrogen evolution using a sacrificial reagent was comparable to SnNb$_2$O$_6$ produced by solid-state synthesis. There are many controllable factors, such as the choice of the salt, the stoichiometric mixture, the heating temperature and the reaction time. Therefore, it is important to investigate the effect of flux on the size, shape, crystallinity, and growth of SnNb$_2$O$_6$ to improve the photocatalytic activity. In this work, the effects of the flux ratio and synthesis temperature were investigated on the crystal growth of SnNb$_2$O$_6$ particles. The photocatalytic activity of the materials synthesized by the flux method was compared to the activity of the materials synthesized by the solid-state method. The unique plate-like morphology of the product was obtained by the flux-assisted method, and the separation of excited carriers through these plate-like structures was probed using nanoparticle photo deposition by the reduction of Ag$^+$ and Pt$^{4+}$ cations to Ag and Pt metals, respectively, as electron sites and the oxidation of Pb$^{2+}$ to the PbO$_2$ metal to track holes.

3.2. Results and discussion

3.2.1. Particle crystal structure

Figure 0.1 shows the XRD patterns of the powders prepared by solid state synthesis and by flux-assisted synthesis after being washed and dried. The powders prepared by solid-state synthesis at 800 °C showed the formation of SnNb$_2$O$_6$ with the Froodite structure
(monoclinic) in a pure phase, and all peaks can be indexed from the PDF data (PDF-01-084-1810).\textsuperscript{30}

The synthesis at 800 °C was necessary to obtain the pure phase of SnNb\textsubscript{2}O\textsubscript{6} because of the slow diffusion process during solid state synthesis.\textsuperscript{31} A trace amount of the precursor phases was observed in the XRD pattern for the sample synthesized by the solid-state method at 600 °C for 10 h as shown in Figure 3.2.

![XRD patterns](image)

**Figure 0.1.** The XRD patterns of SnNb\textsubscript{2}O\textsubscript{6} prepared by solid-state synthesis at 800 °C (800-SS) and by flux-assisted synthesis with different reactant (SnO + Nb\textsubscript{2}O\textsubscript{5}) : flux (SnCl\textsubscript{2})
molar ratios: 1:1-F, 1:3-F, 1:6-F, 1:10-F, and 1:14-F. Reference: ICSD (PDF-01-084-1810)\textsuperscript{30}

Figure 3.2. XRD patterns of SnNb\textsubscript{2}O\textsubscript{6} synthesized by solid state synthesis at 600 °C for 10 h. Star shows peaks corresponding to remaining Nb\textsubscript{2}O\textsubscript{5} and square shows SnO\textsubscript{2}.

The XRD pattern of the material synthesized by flux assisted synthesis at 1:1-F showed a low crystalline nature of SnNb\textsubscript{2}O\textsubscript{6} formed with a small amount of the starting material Nb\textsubscript{2}O\textsubscript{5} remaining, indicating that this low flux ratio was not sufficient to form the SnNb\textsubscript{2}O\textsubscript{6} crystal at 600 °C, which may be attributed to the low solubility of the precursors at this flux amount. At 1:3-F and 1:6-F a small amount of the remaining starting material was observed as well, but they become negligible at high flux ratios. As the flux ratio increased,
the peak intensity of the (600) plane exclusively increased, suggesting that the growth of
the (600) plane was preferentially induced by the presence of flux along the (bc) plane.\textsuperscript{27}
This preferential growth can be explained by the presence of chloride ions in the molten
salt, which may complex with Sn\textsuperscript{2+} ions and selectively lower the interfacial energy along
this plane, making growth along this plane more favorable at the expense of other
planes.\textsuperscript{32,33} The crystallinity of the main peaks increased with increasing flux ratio, and an
almost pure phase was obtained at the highest ratios, (1 : 10) and (1 : 14), with only a trace
amount of the remaining starting materials (2\% estimated from the Rietveld analysis). This
result confirms the beneficial effects of flux-assisted synthesis in that it leads to the desired
products at lower temperatures than solid-state synthesis with the specific ability to induce
preferential crystal growth by modifying the flux parameter. This ability is explained by
the improved extent of dissolution of the precursors in the molten salt when the flux
quantity was increased. To study the effect of temperature on the growth of the material,
synthesis experiments were conducted at lower temperatures (300 and 500 °C). At 500 °C,
as the flux ratio increases from 1:1 to 1:14, the crystallinity of the main peaks also
increases, and a single phase of SnNb\textsubscript{2}O\textsubscript{6} was observed at high ratios (Figure 3.3).
Figure 3.3. XRD patterns of SnNb$_2$O$_6$ synthesized by molten salt flux method at 500 °C for 10 h with different (SnO,Nb$_2$O$_5$ : SnCl$_2$) ratios, a) 1:1, b) 1:3, c)1:6, d) 1:10.

The synthesis of single-phase SnNb$_2$O$_6$ was incomplete at 300 °C with ratios of 1 : 1-F, 1 : 3-F, and 1 : 6-F, and the XRD patterns show the main peaks of Nb$_2$O$_5$ and a mixture of SnO, SnO$_2$ and metallic Sn. Interestingly, even at a low temperature (300 °C), for the materials synthesized at a high flux ratio (1 : 10-F), the SnNb$_2$O$_6$ crystal phase was obtained with low crystallinity and remaining precursors (Figure 3.4). Also the longer synthesis time (30 h) led to the enhanced crystallinity of SnNb$_2$O$_6$ (Figure 3.4). This result suggests that the SnCl$_2$ flux functions as the solution medium, lowering the chemical potential of the reactants to reach the liquid single-phase region.
Figure 0.4. XRD patterns of SnNb$_2$O$_6$ synthesized by molten salt flux method at 300 °C for 10 h with (SnO,Nb$_2$O$_5$ : SnCl$_2$) ratios of a) 1:1, b) 1:3, c) 1:6, d) 1:10 for 10 h. and the sample synthesized for 30 h e) 1:10-F for 30 h (* Nb$_2$O$_5$, SnO$_2$, Sn, SnNb$_2$O$_6$).

In this region of the phase diagram, it is anticipated that both reactants (SnO + Nb$_2$O$_5$) dissolve and their mobility increases.$^{25}$ The nucleation of the SnNb$_2$O$_6$ product may begin in the liquid phase under high supersaturation, known as the solution precipitation mechanism.$^{34}$ After nucleation, the obtained product continues to grow. The best known mechanism of growth is the Ostwald ripening,$^{35}$ the rate of which depends on the diffusion coefficient, the solubility, and the atomic structure.$^{35}$ A high diffusion coefficient and higher solubility of starting materials are generally attained at higher temperatures and higher ratios of the flux salt. As discussed, the formation of SnNb$_2$O$_6$ was preferred at higher temperatures and higher flux ratios, consistent with this mechanism.
3.2.2. A morphological analysis

The morphology of semiconductor particles is affected by both the equilibrium and growth forms of the crystal.\textsuperscript{36} The crystal structure generally determines the stable facets, and the particle shape is also influenced by the chemical composition of the crystal and the salt. The particles tend to grow towards equilibrium by minimizing the surface free energy, which is achieved mainly by dissolving the planes with high surface energy and growing the more stable planes. This process results in an anisotropic growth along these low energy stable faces, which will have a lower growth rate and consequently afford well-developed facets.\textsuperscript{32} To evaluate the effect of flux on the SnNb$_2$O$_6$ morphologies, SEM images of the products synthesized by both methods were compared. Figure 3.5. shows the SEM images of SnNb$_2$O$_6$ synthesized by the molten salt flux-assisted method and by solid-state synthesis.
Figure 0.5. SEM images of SnNb$_2$O$_6$ prepared by solid-state synthesis at 800 °C (800-SS) and by flux-assisted synthesis with different reactant (SnO + Nb$_2$O$_5$) : flux (SnCl$_2$) molar ratios: 1 : 1-F, 1 : 3-F, 1 : 6-F, 1 : 10-F and 1 : 14-F.

The effect of the reactant to flux molar ratio can be clearly observed. At a low reactant to flux ratio (1: 1), the obtained product began showing plate morphology, but with a limited anisotropic growth in the 2D, which afforded aggregates with non-uniform particles ranging between 100 and 500 nm. This result can be explained by the lower solubility of the reactant particles at this low flux ratio. However, in the 1: 3-F sample, the plate morphology was clearer and better defined, and the plate size was between 500 nm and 1 mm in length with a thickness of approximately 100 nm. At higher ratios (1: 6-F, 1: 10-F, and 1: 14-F), large plates with lengths of 0.5–2 mm and thicknesses of approximately 100 nm were obtained. The increase in the particle size is explained by the Ostwald ripening mechanism as prolonged heating at a higher flux ratio will increase the mobility and therefore the diffusion coefficient of the reactants. This results in a higher growth rate and a larger particle size. The SEM of 800-SS confirms that the materials synthesized by the solid-state method showed irregular grain particles that form aggregates with increased grain boundaries. The sintering of the product particles synthesized by the solid-state method begins simultaneously with the formation of particles. This sintering can be avoided by the flux-assisted method, as the molten salt covers the surfaces of all particles and inhibits their agglomeration. This advantage becomes more evident at high flux ratios, as it can be observed that the plates in the 1: 6-F and 1: 10-F samples have more uniform surfaces with fewer aggregates of small particles than 1:3-F and 1:1-F. The trend of the particle growth and plate-like morphology was similarly observed in the lower-temperature synthesis (500 °C; Figure 3.6.). However, it can be clearly observed that the
large plate-like particles have smaller plates on their surface at the ratios of 1: 1-F, 1:3-F, and 1 : 6-F. This result is explained by the lower growth rate at lower temperature and indicates that the obtained morphology is a consequence of the molten salt flux.

Figure 3.6. SEM images of SnNb2O6 synthesized by molten salt flux method with (SnO,Nb2O5 : SnCl2) ratios of a) 1:1, b) 1:3, c)1:6, d) 1:10 at 500 °C.

The particle size was estimated from the SEM images, and the results are summarized in Table 3.1. The BET surface areas of the synthesized materials are summarized in Table 3.1 as well. The material prepared by solid-state synthesis (800-SS) showed a surface area of 1.3 m².g⁻¹, similar to the reported value.¹⁶ The samples synthesized by the flux-assisted method showed BET surface areas of 6.1, 4.1, 6.6, 5.2, and 4.4 m².g⁻¹ for 1 : 1-F, 1 : 3-F, 1 : 6-F, 1 : 10-F, and 1–14-F, respectively. Figure 3.7. shows the diffuse reflectance UV-Vis spectra of SnNb2O6 synthesized at different flux ratios (1 : 1-F to 1 : 14-F) and in the solid
state (800-SS). It can be seen that the samples prepared by the flux-assisted method show higher surface areas than the samples synthesized by the solid-state method, but the difference is not very large due to the similar particle sizes. SnNb$_2$O$_6$ powders prepared by the flux-assisted method have band gaps of 2.1, 2.46, 2.44, 2.45, and 2.45 eV for 1 : 1-F, 1 : 3-F, 1 : 6-F, 1 : 10-F, and 1 : 14-F, respectively, as summarized in Table 3.1. The sample prepared by solid-state synthesis (800-SS) has a band gap of approximately 2.33 eV, which also agrees with previous reports.$^{15}$

Figure 0.7. A) DR-UV-Vis spectra of SnNb$_2$O$_6$ prepared by solid-state synthesis at 800 °C (800-SS) and by flux-assisted synthesis with different reactant (SnO + Nb$_2$O$_5$) : flux (SnCl$_2$) molar ratios: 1 : 1-F, 1 : 3-F, 1 : 6-F, 1 : 10-F, and 1 : 14-F. B) Tauc’s plots of SnNb$_2$O$_6$ synthesized by the molten salt flux method with (SnO,Nb$_2$O$_5$ : SnCl$_2$) ratios of a) 1:1, b) 1:3, c) 1:6, d) 1:10 at 600 °C and of the sample prepared by solid state method e) 800-SS.
The distinctive absorption edges were observed in all cases, except for the sample with 1:1-F. For the 1:1-F sample, a slight red-shift in the absorption edge can be attributed to the presence of defects, as observed in XRD, where the unreacted precursors were still present (Figure 3.1.). As the flux ratio increased, the absorption edge was slightly blue-shifted. The absorption beyond the band gap of SnNb₂O₆ (baseline) decreased and was the lowest for the 1:10-F sample, which may imply a decrease in reduced species or defects. This minor band gap alteration (blue-shift) with intensive flux use may be correlated with improved plate-like morphology, where the crystal shows a 2D anisotropy while decreasing the thickness with respect to the length. This blue shift was previously reported for the synthesis of Bi₂MoO₆ materials with a nanoplate-like morphology.³⁸

Table 3.1. The synthesis temperature, Sn/Nb ratio from ICP, average particle size estimated from SEM images, and BET surface area for the samples synthesized at different flux ratios.

<table>
<thead>
<tr>
<th>Reactant molar ratio (SnO-Nb₂O₅) : SnCl₅</th>
<th>Band gap (eV)</th>
<th>Sn/Nb (ratio)</th>
<th>Average particle size (μm)</th>
<th>Surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>2.1</td>
<td>0.49</td>
<td>0.3</td>
<td>6.1</td>
</tr>
<tr>
<td>1:3</td>
<td>2.46</td>
<td>0.49</td>
<td>0.5-1</td>
<td>4.1</td>
</tr>
<tr>
<td>1:6</td>
<td>2.44</td>
<td>0.49</td>
<td>1.5-2.0</td>
<td>6.6</td>
</tr>
<tr>
<td>1:10</td>
<td>2.45</td>
<td>0.49</td>
<td>1.5-2.0</td>
<td>5.2</td>
</tr>
<tr>
<td>1:14</td>
<td>2.45</td>
<td>0.55</td>
<td>2.0-3.0</td>
<td>4.4</td>
</tr>
<tr>
<td>800-SS</td>
<td>2.33</td>
<td>-</td>
<td>0.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>
The Raman spectra of these samples were compared (Figure 3.8.), and they all showed the same Raman shifts for Nb–O bonds, which further confirm that the blue-shift is due to the plate morphology rather than structural differences. The band gaps of these materials were estimated from Tauc’s plot (Figure 3.7. B and it was observed that the absorption edges of the samples from 1:3-F to 1:14-F are steep, indicating the transition from the valence to the conduction band.

Figure 3.8. Raman spectra of SnNb$_2$O$_6$ synthesized by molten salt flux method with (SnO,Nb$_2$O$_5$ : SnCl$_2$) ratios of a) 1:1, b) 1:3, c) 1:6, d) 1:10 and of the sample prepared by solid state method e) 800-SS.
3.2.3. Surface properties

Surface is an important parameter in designing any photocatalyst since all chemical reactions take place on it. To study the effect of flux on the surface, XPS measurements were conducted. Figure 4 shows XPS spectra of the 1:10-F sample versus 800-SS.

It was reported that binding energies of Sn 3d₅/₂ of Sn²⁺ (SnO) and Sn⁴⁺ (SnO₂) are 485.8 eV and 486.3 eV, respectively.⁴⁹ A clearer distinction between Sn²⁺ and Sn⁴⁺ is made possible using Auger lines corresponding to the M₄N₄₅N₄₅ transition, showing a difference of about 1.3 eV.⁴⁷–⁵⁰

![XPS spectra](image)

Figure 0.9 XPS spectra of (a) Sn 3d₅/₂ and (b) Sn Auger peaks (M₄N₄₅N₄₅) of SnNb2O6 prepared by solid-state synthesis at 800 °C (800-SS) and by flux assisted synthesis with a reactant (SnO + Nb₂O₅) : flux (SnCl₂) molar ratio of 1 : 10-F.

It can be clearly observed in Figure 3.9. a and b that the 1:10-F sample’s surface is mainly composed of Sn²⁺ whereas 800-SS has a larger amount of Sn⁴⁺. This is explained by the difference in synthesis temperature. The higher temperature employed in solid state synthesis promoted the oxidation of the surface. However, the flux assisted synthesis
enabled the formation of SnNb$_2$O$_6$ at lower temperature which prevented the oxidation of the surface. This emphasizes the positive role of flux synthesis in minimizing surface states and impurities. This effect is quite important since Sn$^{4+}$ species acts as trap states for electrons which can decrease the activity of the material.$^{16}$

### 3.2.4. Photocatalytic properties

Figure 3.10. shows the photocatalytic activity for hydrogen evolution from 10% methanol aqueous solution using synthesized SnNb$_2$O$_6$ photocatalysts. It was observed that as the flux to reactant ratio increased, the photocatalytic activity for hydrogen evolution increased in parallel. The samples with 1:1-F and 1:3-F showed negligible activities (1 and 2.2 mmol h$^{-1}$, respectively). This result may be attributed to the incomplete synthesis of the 1:1-F sample, which can be observed in the DR-UV-Vis spectra (Figure 3.7. A), and the low crystallinity of these two samples, as shown by XRD (Figure 1).
Figure 0.10 Photocatalytic hydrogen evolution activities of SnNb₂O₆ prepared by solid-state synthesis at 800 °C (800-SS) and by flux-assisted synthesis with different reactant (SnO + Nb₂O₅) : flux (SnCl₂) molar ratios: 1:1-F, 1:3-F, 1:6-F, and 1:10-F.

It was observed that the 1:6-F sample gave high hydrogen amount (23 mmol) after 1 h but it decreased after the third hour to become lower than that of 800-SS. The samples prepared at the high flux ratio 1:10-F gave the hydrogen amount of about 34 mmol after 1 h, then reaching 158 mmol of hydrogen after 5 h. This is relatively higher than the 800-SS sample (15 mmol after 1 h and 122 mmol after 5 h). The hydrogen amount with the sample prepared with a high flux ratio of 1:14-F was similar to that with the 1:10-F sample.

The improved hydrogen evolution activity can be explained by two factors. The first is the smoother surfaces with minimized grain boundaries obtained by the molten salt flux-assisted method in comparison with the agglomerated particles obtained by the solid-state method. Grain boundaries are generally considered to be electron recombination sites. The second is the enhanced surface properties produced by the flux-assisted method, which afforded less oxidized surfaces. As discussed in the XPS section, the Sn⁴⁺ sites create local electronic states that are disconnected from the bulk (Sn²⁺), thus functioning as trap sites for excited carriers. The same trend for hydrogen evolution activity was observed at the lower temperature of 500 °C.

This result emphasizes the role of the flux ratio as a control parameter for photocatalytic performance. To further confirm that the difference in photocatalytic activity does not originate from any difference in the composition of the samples, ICP quantitative analysis was performed. The results are summarized in Table 3.1. All the prepared samples have the same Sn/Nb ratio of 0.49, which nearly matches the theoretical ratio of 0.5. This result
is consistent with the lack of extra Sn species from excess flux. It is important to note that the Froodite SnNb$_2$O$_6$ crystal structure is known to be a layered material, as shown in Figure 3.11.

Figure 3.11. Polyhedral model structures of SnNb$_2$O$_6$; Sn (purple sphere) and O (red sphere) with Nb-centered coordinate (green octahedra).

The crystal structure is made up of Nb$_2$O$_6$ edge-shared octahedra forming a two-octahedron-thick sheet with Sn$^{2+}$ ions interlayered between the two sheets. Layered materials have been introduced by Domen and coworkers as a unique class of heterogeneous photocatalysts called “Two-Dimensional” photocatalysts $^{40-42}$ They showed a different behavior from the conventional bulk semiconductor catalysts and were able to achieve overall water splitting using K$_4$Nb$_6$O$_{17}$ as the photocatalyst and nickel oxide as the cocatalyst. These materials have the advantage of having two types of periodic
interlayers, called Interlayer I and Interlayer II. This structure allows water molecules to intercalate within the interlayers such that the reduction of water to hydrogen takes place on one side of the NbO$_6$ sheet (Interlayer I), while the oxidation of water takes place on the other side of the NbO$_6$ octahedra (Interlayer II). Adding ultrafine nickel particles as a hydrogen evolution cocatalyst within the interlayers enhanced the activity of the material by improving the extent of charge separation and minimizing electron–hole recombination.\textsuperscript{43} Another family of layered materials called ion-exchangeable niobates with the general form of A(M$_{n-1}$Nb$_n$O$_{3n+1}$), where A = Na, K, Rb, Cs; M = La, Ca, was found to show improved photocatalytic activity.\textsuperscript{43} This perovskite family has the ability to exchange alkaline metal ions with H$^+$ ions. This improved hydrogen evolution activity was attributed to the enhancement in the migration of reactant molecules within the interlayers.\textsuperscript{43}

As concluded from XRD, the molten salt did lead to preferential growth along the (b,c) plane, which resulted in the plate-like morphology visible by SEM. Based on the similarity of structure between tin niobate materials and the reported layered materials, the effect of this anisotropic growth was investigated on the charge separation mechanism. To probe the electron-hole pair in this material, the photo-deposition of Ag, Pt, and PbO$_x$ was examined by HR-STEM. It is known that under visible radiation, Pt$^{4+}$ and Ag$^+$ will be photo-reduced into Pt and Ag metal nanoparticles, respectively, and they will act as electron acceptors, while Pb$^{2+}$ will be oxidized into PbO$_2$ and act as a hole acceptor.\textsuperscript{29} Therefore, probing these metals/metal oxides on the surface of a semiconductor will provide insight into the active sites.\textsuperscript{44} Three photo-depositions were performed: 1) photo-reduction of Ag$^+$ to track
electrons, 2) photo-oxidation of Pb\(^{2+}\) to probe holes, and 3) simultaneous photo-oxidation of Pb\(^{2+}\) and photo-reduction of Pt\(^{4+}\).

Figure 03.12. TEM images of (a) SnNb\(_2\)O\(_6\) deposited with Ag particles, (b), (c) HRTEM of SnNb\(_2\)O\(_6\) with Ag nanoparticles, (d) SAED of (c), (e) SnNb\(_2\)O\(_6\) deposited with PbO\(_x\) and (f) SnNb\(_2\)O\(_6\) deposited with Pt and PbO\(_x\) simultaneously.
Figure 3.12. shows HR-STEM micrographs, generated by using an high angle annular dark field (HAADF) detector that was attached above the projection chamber of the microscope, of SnNb$_2$O$_6$ with silver nanoparticles (a, b, c), PbO$_2$ (e) and both Pt and Pb (f). The surface of SnNb$_2$O$_6$ deposited with Ag shows a uniform morphology with minimum aggregates and a homogenous distribution of Ag Figure 3.12. This uniform distribution of Ag nanoparticles is more obvious at higher magnification (Figure 3.12. b). This result suggests that the smooth morphology of the surface minimizes electron-hole recombination and enhances the activity of SnNb$_2$O$_6$ by providing homogenously distributed active sites with minimum grain boundaries. The EFTEM mapping of Ag on 1:10-F sample (Figure 3.13. a) clearly shows the uniform distribution of silver nanoparticles on surface and edges.

Figure 3.13. (a) HR-STEM image of SnNb$_2$O$_6$ deposited with Ag particles, (b) EFTEM mapping of (a), (c) HR-STEM of SnNb$_2$O$_6$ with Pt and PbO$_x$ nanoparticles, (d) EFTEM mapping of (c).
By comparison with 800-SS sample deposited with Ag (Figure 3.14), it can be clearly observed that silver distribution is less uniform and large aggregates of silver nanoparticles (size around 10 nm) are observed. This further confirms that 800-SS non uniform morphology affects the distribution of the active sites for hydrogen evolution and electrons pathway.

![HRTEM images of 800-SS samples deposited with a) Ag and b) PbO\textsubscript{x}](image)

Figure 3.14. HRTEM images of 800-SS samples deposited with a) Ag and b) PbO\textsubscript{x}

Figure 3.12.c shows HR-STEM micrographs of SnNb\textsubscript{2}O\textsubscript{6} deposited with silver, where clear lattice fringes are observed. Figure 3.13.d shows the corresponding fast Fourier transform (FFT), which contain the frequencies of 0.35, 0.237 and 0.255nm. These frequencies present correspond to (-111), (020) and (002) inter-planer d-spacings of the monoclinic SnNb\textsubscript{2}O\textsubscript{6} structure, respectively. It shows that the sample has single-crystalline character. Furthermore, the symmetry of the FFT shows that the crystal was oriented along the [110] zone-axis with respect to the direction of electron beam. Figure 3.12.e shows the sample on which the photo-oxidation of PbO\textsubscript{x} occurred in the presence of iodate as the electron acceptor. It can be observed that PbO\textsubscript{x} deposited randomly on the surface. It was further
confirmed by Energy Dispersive Spectroscopy (EDS) that Pb species are present at various positions on the surface (Figure 3.15.c and d), and there was no observed selective photodeposition of PbO<sub>x</sub>. Similar behavior was observed in 800-SS deposited with PbO<sub>x</sub> where the PbO<sub>x</sub> nanoparticles were deposited on the surface as well as on edges (Figure 3.14.). When both Pt and Pb were present in the reaction medium, it was determined from the EDS spectra that Pt predominates on the surface (Figure 3.15.d) It can be observed that Pt is deposited on both sets of planes (600) and (-311) with d-spacings of 0.29 and 0.34 nm, respectively.

![Figure 3.15.](image)

Figure 3.15. (a) 1:10-F sample deposited with Pt and PbO<sub>x</sub>, b) only PbO<sub>x</sub>, (c,d) are corresponding EDS spectra respectively.
EFTEM elemental mapping was conducted to further confirm the distribution of Pt and PbO\textsubscript{x} nanoparticles on surface of 1:10-F. Figure 3.14.c shows the EFTEM elemental mapping of sample deposited with both Pt and PbO\textsubscript{x}. It can be clearly observed that Pt (green) and PbO\textsubscript{x} (red) deposit randomly on the surface next to each other with no special separation or selective deposition. This observation indicates that there was no selective charge separation on specific facets, and therefore, the morphology obtained by the flux-assisted method did not affect the charge separation mechanism in these layered materials. This result confirms that the role of flux is mainly in promoting the growth of the plate-like morphology with non-aggregated surfaces, and the preferential growth has no effect on the crystal structure and distribution of active sites for photocatalysis.

3.3. Experimental

3.3.1. Synthesis of SnNb\textsubscript{2}O\textsubscript{6}

Stoichiometric molar quantities of SnO (Sigma Aldrich, 99.99%) and Nb\textsubscript{2}O\textsubscript{5} (Aldrich, 99.99%) were mixed homogenously by grinding for 20 min under an argon atmosphere. SnCl\textsubscript{2} (Aldrich, 99.99%) was added as a flux to provide different reactant to flux molar ratios (1:1-F, 1:3-F, 1:6-F, 1:10-F, 1:14-F, F stands for flux). The mixture was ground again for 10 min under an argon atmosphere. The obtained mixture was transferred to an alumina boat and heated inside a tubular furnace under nitrogen flow with a flow rate of 100 ml min\textsuperscript{-1}. Different reaction temperatures (300, 500, 600 °C) were tested for 10 h, followed by radiative cooling to room temperature. The obtained samples were then washed by stirring overnight in Milli-Q water (18.2 MΩ cm\textsuperscript{-1}) to remove the remaining
flux SnCl$_2$. The obtained powders were dried at 70 °C. Solid-state synthesis was performed by grinding for 30 min and heating for 10 h at 800 °C, as reported previously.$^{15}$

### 3.3.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded with a BRUKER D8 Advance diffractometer (DMAX 2500) using a Cu K$_\alpha$ energy source at 40 kV and 40 mA. Scanning Electron Microscopy characterizations were performed on a Nova Nano 630 scanning electron microscope (SEM) from FEI company. The electron beam energy was set to 5 keV before the start of analysis. SEM measurements were used to determine the morphology as well as particle size of the synthesized particles. The SEM specimens were prepared by suspending them in ethanol and dispersing them by sonication. A drop of the solution was then poured onto the SEM stub and was dried before observations. The N$_2$ sorption studies were conducted using a Micrometrics ASAP 2420 to determine the Brunauer-Emmett-Teller (BET) surface area. The ICP measurements were performed using an ICP-OES Varian 72 ES. Digestion of the material was performed in the microwave digestion milestone of model ETHOS1. Diffuse reflectance spectra were measured using a UV-Vis spectrometer with an integrating sphere (JASCO, U-best 570) and were demonstrated according to the Kubelka-Munk function. Raman spectra of SnNb$_2$O$_6$ were acquired using a NT-MDT NTEGRA nano- and micro-Raman spectrometer equipped with a He-Ne laser ($\lambda=633$ nm), two solid-state lasers ($\lambda=532$ nm and 473 nm) and a Peltier cooled CCD Andor iDus 420. All spectra were acquired using 532 nm as the exciting wavelength in the z(x,x)-z backscattering geometry. For X-ray
photoelectron spectroscopy (XPS), an AMICUS/ESCA 3400 instrument from KRATOS analytical was used with dual Mg/Al anodes and an energy source at 12 kV and 10 mA, based on calibration against the carbon 1s photoelectron signal at 284.2 eV. Transmission electron microscopy (TEM) analysis of samples was also performed to investigate the crystal structure, particle size and elemental composition present in the samples. The TEM analysis was carried out by setting the microscope in scanning TEM (STEM) and was accomplished by employing an aberration corrected Scanning TEM (STEM) microscope of model Titan G² 60-300-ST from FEI Company. The microscope was operated at 300 keV beam energy during the STEM investigations and was the coefficient of spherical aberration of Condenser-2 lens was reduced to about 1 um to perform a high-resolution STEM analysis of the samples. The Fast-Fourier transform (FFT) analysis of the acquired micrographs were also calculated to measure the interplanar d-spacings of the crystalline phases present in the samples. The entire STEM analysis was performed in Gatan Microscopy Suite (GMS v. 1.83) software package from Gatan, Inc.

Elemental mapping was performed by using a post-column energy filter of model GIF Tridiem 863 from Gatan, Inc. The microscope was set to EFTEM mode to reduce the image magnification so that the field-of-view on the GIF CCD is about the same as that of the image-plane of the pre-GIF CCD. The elemental maps are generated by using the Ag-N23, Nb-N23, Pt-O23, and Pb-O23 energy edges from the corresponding Ag, Nb, Pt, and Pb elements, respectively. Furthermore the so called jump-ratio method was employed to produce these maps.
3.3.3. Photocatalytic experiments

Hydrogen evolution experiments were performed using a recirculating reactor unit. The accumulated gaseous products were analyzed using a Shimadzu GC with a Molecular Sieve 5A column. Photocatalytic overall water splitting was performed under visible light irradiation using a 300 W Xe lamp (CM1) with cutoff filter L42 with wavelength range (420 < λ < 1100nm) (Fig. S8). The experiments were performed using 90 ml of H₂O, 10 ml of methanol and 100 mg of photocatalyst. Wet impregnation was used to load 1 wt% platinum from an aqueous solution of H₂PtCl₆. The sample was heated while stirring until the water completely evaporated. The obtained product was reduced under hydrogen flow at 250 °C for 1 h.

3.3.4. Photo-deposition of metals and/or oxides

Three types of depositions were conducted: single photo-reduction, single photo-oxidation, and simultaneous photo-oxidation and photo-reduction. All photo-depositions were performed similarly in the recirculating reactor unit in 100 ml of Milli-Q water and irradiated by a 300 W Xe lamp (CM1) with cutoff filter L42 (420 < λ < 1100nm) under continuous stirring. After 10 h of photo-deposition, the obtained suspension was filtered and washed with Milli-Q water, then dried at 70 °C for 12 h. The resulting powders were examined by HR-STEM.

The photo-reduction of Ag nanoparticles was performed starting with 0.1 g of SnNb₂O₆ and 10 mM AgNO₃ solution with 0.2 g of La₂O₃ as a buffer to maintain an alkaline medium. The photo-oxidation of PbOₓ was performed starting with aqueous Pb
(NO₃)₂ solution as a precursor in the presence of NaIO₃ as an oxidizing agent. The simultaneous photo-deposition of both PbOₓ and Pt was achieved using 5 wt% Pb (NO₃)₂ and H₂PtCl₆ combined, with respect to the SnNb₂O₆ material.²⁹
3.4. Summary

In this chapter, the role of flux-assisted synthesis using a molten salt has been investigated as a means to control the surface properties. The crystal morphology was successfully tuned by increasing the flux to reactant molar ratio, which afforded defined particles with non-aggregated surfaces. The XRD patterns and SEM analyses confirmed a 2D anisotropic growth along the bc plane, providing a plate-like morphology as the flux ratio increased. The DR-UV-Vis spectra of the obtained samples were consistent with the formation of SnNb$_2$O$_6$ in a single phase. The photocatalytic activity for hydrogen evolution was enhanced as the flux ratio was increased, reaching the highest value at a 1:10-F ratio. This result was explained by the beneficial role of increased flux in allowing the formation of tin niobate at a lower reaction temperature compared with solid-state synthesis. This heightened activity coincides with the minimized amount of Sn$^{4+}$ on the surface boundaries, which may act as trap states. Furthermore, the flux-assisted method resulted in plate-like morphology with minimal aggregates. The molten salt flux-assisted synthesis provides a margin for control over surface properties, morphology, and defects that could increase the photocatalytic activity.
3.5. References

CHAPTER 4

UV-Vis optoelectronic properties of α-SnWO₄: A comparative experimental and density functional theory based study

This chapter discusses the synthesis of α and β phases of SnWO₄ using flux assisted method. This method enabled the synthesis of the pure β SnWO₄ at 670 °C which is lower temperature than solid state synthesis 800 °C. Band gaps of 2.05 and 2.9 eV were obtained for α and β SnWO₄, respectively. The low band gap of the α-SnWO₄ is interesting. Hence, the next step was the deposition of α-SnWO₄ thin film as a photoanode for solar water splitting. The thin films were synthesized by using direct current (DC) magnetron sputtering with simultaneous depositions of tin and tungsten in reactive conditions. Appropriate annealing treatment was needed to obtain pure phase. The structural characterizations were performed by using X-ray diffraction, and scanning electron microscopy. Optical properties are evaluated by UV-Visible transmittance and reflectance measurements. Photoelectrodes were fabricated and tested for photoelectrochemical (PEC) performances in aqueous solution under solar irradiation (AM 1.5 G). The α-SnWO₄ samples absorb solar irradiation up to 800 nm with an indirect bandgap.

The combined theoretical approach was applied to determine the optoelectronic properties of the α-SnWO₄ for UV-Vis excitation. The experimentally measured values for thin films were systematically compared with high-accuracy density functional theory and density functional perturbation theory using the HSE06 functional. The α-SnWO₄ material shows

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3 This chapter was adapted from A. Ziani, M. Harb, D. Noureldine, K. Takanabe, APL Mater. 2015, 3, 096101.
an indirect band gap of 1.52 eV with high absorption coefficient in the visible-light range ($>2 \times 10^5$ cm$^{-1}$). The results show relatively high dielectric constant ($>30$) and weak diffusion properties (large effective masses) of excited carriers. Low onset potential of $\alpha$-SnWO$_4$ suggests that the material can be a good candidate for the efficient photoanode if the transport properties are enhanced.
4.1. Introduction

Due to the tremendous price fluctuation of fossil fuels and the consequent environmental problems such as global warming, it is necessary to develop energy systems that convert renewable energies to generate clean fuels and chemicals in a large quantity. Hydrogen (H₂) is a candidate for future energy carrier which is clean and carbon neutral hence it may solve current environmental problem. Solar water splitting technology utilizes the most abundant source, water, as a reactant combined with the most accessible energy resource, sunlight, to produce clean fuel. This reaction involves many fundamental mechanisms, starting from solar light absorption, followed by electron-hole pair generation/dissociation, charge carriers’ diffusion, and finally ending in the water redox reactions for oxygen (O₂) and H₂ generation.¹⁻⁸

For this sustainable energy conversion, it is necessary to develop highly efficient photocatalyst or photoelectrode to decompose water for O₂ and H₂. Titanium oxide (TiO₂)⁹ and lanthanum-doped sodium tantalum oxide (NaTaO₃)¹⁰ materials are well known to be able to perform overall water splitting but only under UV irradiation because of their wide bandgap (E₉>3.2 eV). However to increase the efficiency of the reaction, absorption should be shifted to the visible region. Visible light photoactive oxide in the 2.0 - 2.8 eV range like hematite (α-Fe₂O₃)¹¹,¹² bismuth vanadate (BiVO₄),¹³,¹⁴ or tungsten oxide (WO₃)¹⁵,¹⁶ are the most used material and they are promising photocatalytic components for solar water oxidation. They can absorb solar irradiation in the visible region, but they are considered to be suitable only for half-reactions (oxidation). However, those materials are still presenting an high onset potential versus reversible hydrogen electrode (vs. RHE), indicating that extra bias or another photocathode material is essential to achieve water
oxidation using this system. Oxy-nitrides metal or perovskites materials are reported to be able to perform overall water splitting. Due to their good visible light absorption, and its ability for redox reaction, tantalum nitride (Ta₃N₅) is one of the most attractive photocatalyst. Significant photocurrent can be achieved by increasing the nanostructuration of the photocatalyst or by using performant co-catalyst. However, as was reported recently, Ta₃N₅ suffers from weak diffusion properties. Despite that it presents good absorption and charge carriers’ extraction. The high applied over-potential still remains a challenge and it is important to look for other possible candidate material, easy to synthesize and control the chemical compositions. New chemical phases in the tungsten-based materials are modified by the addition of second metal like zinc (Zn²⁺), silver (Ag⁺), bismuth (Bi³⁺) or tin (Sn²⁺) and proved to shift the onset potential into less than 0 V vs. RHE. Among them, Sn²⁺ incorporation into the structure can produce new tin tungstate (SnWO₄) material phase which have extended visible-light-response due to the s² orbitals Sn²⁺ contribution into the valence band. Its structure is composed of safe and relatively abundant chemical elements. SnWO₄ presents two polymorphs which have distinct properties. The first polymorph is with alpha (α-) phase orthorhombic structure that can be formed at low temperatures. The second phase is beta (β-) phase cubic structure, the synthesis of which requires relatively high temperatures with appropriate quenching to prevent the phase transition into the α-phase. In terms of band positions of SnWO₄, both phases were reported with an onset potential of 0 V vs. RHE deduced from Mott–Schottky (MS) measurements. Although many research works reported β-SnWO₄ as the more photocatalytically active phase compared to α-SnWO₄ during organic dyes degradation.
In most of the previous reports, SnWO$_4$ is synthesized by chemical synthesis such as solid state method, wet chemistry or by precipitation method using electrostatic destabilization. A few research works by Solis et al. developed this material with sputtering technique for gas-sensing application in the nineties. More recently, Pyper et al. reported a WO$_3$ thin film conversion to SnWO$_4$ by hydrothermal synthesis. In this last work, they report the weak PEC performance of the $\alpha$-phase of SnWO$_4$. They attribute this weak photocurrent response to the quick recombination of charge carriers facilitated with the sponge-like structure that permit conductive surface exposition. The preparation of such $\alpha$-SnWO$_4$ photoanode with sputtering technique in the form of dense thin films is a useful approach for the construction of high crystalline quality that may effectively increase the efficiency of the process as well as the chemical stability of the photoelectrochemical (PEC) system. Thin film configuration also allows deep characterization of the photophysical properties of the material. Absorption coefficient estimate the photon number can be cached by certain material amount, dielectric constant gives the charge carriers separation of the material, and electron/hole effective mass indicates the transport quality. Indeed, the knowledge of the semiconductor’s intrinsic properties can predict the PEC performance because the PEC performances are strongly reflected by the intrinsic transport properties of the material. Good experimental characterization and theoretical calculations of those parameters can help to predict the PEC performance of the photoanode.

In this study, powders SnWO$_4$ ($\alpha$ and $\beta$) phases were synthesized by the flux-assisted method for the first time. Single phase highly crystalline SnWO$_4$ material were obtained at lower temperature than solid state synthesis. Then a detailed experimental and theoretical
investigation of the photophysical properties of α-SnWO₄ was conducted. The sputtered thin film configuration allows the accurate determination of its absorption coefficient, dielectric constant, and charge carrier effective masses. These experimental characterizations were systematically compared with first-principles calculations on the basis of density functional theory (DFT, including the perturbation approach DFPT) and employing the range-separated hybrid HSE06 exchange-correlation functional. The choice of the HSE06 functional was based on previous reports on widely used semiconductors in photocatalysis and photovoltaics, showing the high prediction accuracy when compared to experimental data. This systematic study on α-SnWO₄ has never been reported in previous published works.

### 4.2. Results and discussion

#### 4.2.1. Flux assisted synthesis of α and β SnWO₄

Figure 4.1. shows the XRD patterns of SnWO₄ powders at 800 °C with no quenching by solid state method (SnWO₄ –SS) and flux-assisted method (A), β SnWO₄ powders quenched at 800 °C (B), and β SnWO₄ powders quenched at 670 °C (C) in comparison with the reference patterns for both phases.

By comparison between the samples synthesized at 800 °C with no quenching, both the solid state and flux-assisted synthesis resulted in α SnWO₄ as a major phase with minor β SnWO₄ (phase denoted by asterisk). However, the using solid state synthesis an additional impurity SnW₃O₉ is obtained with minor SnO₂ amount. This indicates that the flux-assisted
synthesis favors the formation of single phase material and minimizes the formation of Sn$^{4+}$ oxide, SnO$_2$.

Figure 4.1. XRD patterns of SnWO$_4$ powders synthesized by solid state method (SnWO$_4$-SS) and by flux assisted method with no quenching at 800 °C (A) and quenching at 800 °C and 670°C for B and C respectively. The reference pattern for the two phases are added for comparison.

Another important role of the flux is that it allows the formation of the target product at lower temperature and shortened reaction time.$^{54}$ This is indeed beneficial for Sn$^{2+}$-based compounds, as it results in less oxidized surface where the Sn$^{4+}$ is reported to act as recombination sites.$^{54}$
The synthesis of the β-SnWO₄ powders is reported to be challenging. This involves rapid quenching of the reaction medium from the reaction temperature to room temperature in order to prevent the phase transition which occurs around 670 °C. This limits the reproducible synthesis of β SnWO₄ and often creates impurity (SnO₂ and SnW₃O₉) and α SnWO₄ as secondary phase. These impurities are detrimental for the photocatalytic activity of the material. Therefore, the β SnWO₄ powders were synthesized using the flux assisted method. From figure 4.1, it can be observed that β SnWO₄ is successfully obtained by the flux assisted method at both temperatures. However, by carefully examining the modified region (Figure 4.2), it can be seen that α SnWO₄ and SnW₃O₉ are observed only in the sample synthesized at 800 °C while pure phase β SnWO₄ material was obtained at 670 °C. This reflects the beneficial role of the flux in the synthesis of pure phase material. It is

Figure 4.2. Magnified region of the XRD patterns of the β SnWO₄ powders synthesized by flux assisted synthesis at 670 and 800 °C.
worth to mention that lowering the reaction temperature below the 670 °C which is the phase transition temperature resulted in α SnWO₄ mainly. Other attempts to study different flux material such as Na₂CO₃ and NaCl/KCl mixture were conducted, but were unsuccessful since Na⁺ favors to replace Sn²⁺ and forming Na₂W₂O₇.

Having synthesized the pure phases of α SnWO₄ and β SnWO₄, it is interesting to study absorption properties. Figure 4.3. shows the DR. UV-Vis spectra of the α-SnWO₄ and β SnWO₄. It can be seen that both phases show a visible light absorption however the α-SnWO₄ shows an extended absorption in the visible region to around 700 nm. Comparing the absorption edges, it can be seen the β SnWO₄ exhibits steep absorption edges which is not the case for α SnWO₄. This suggests that the beta phase have direct nature of band gap whereas the alfa phase has indirect bandgap.

![Figure 4.3. DR.UV-Vis spectra of α and β SnWO₄ powders.](image-url)
Figure 4.4. Tauc plots of $\alpha$ SnWO$_4$ powders with direct (a) and indirect (b) bandgaps; and for the $\beta$ SnWO$_4$ powders with direct (c) and indirect (d) band gaps.

Figure 4.4. shows the Tauc plot that are corresponding to the above absorption spectra.

Narrow band gaps are obtained for $\alpha$ SnWO$_4$ ~ 2.0 eV for direct band gap and 1.8 eV for indirect band gaps. However larger band gaps are obtained for the $\beta$ SnWO$_4$ powders with around 3.0 eV for the direct band gap and around 2.1 eV indirect band gap.

Indeed $\alpha$ SnWO$_4$ is more interesting to study as it meets the target band gap as described in (chapter 1) ~ 2.0 eV. Therefore, the understanding the optoelectronic properties of thin films of this material is crucial to understand.
4.2.2. Crystal structure of the α-SnWO₄ films

SnWO₄ films were deposited by direct current magnetron sputtering using W and SnO₂ targets. SnWO₄ thin films were synthesized on FTO and FG substrates with measured thicknesses of 80, 180 and 350 nm, samples denoted as SnWO₄-(80), SnWO₄-(180), and SnWO₄-(350), respectively. The crystal structures of the obtained films were characterized by XRD analysis, and the results are presented in Figure 4.6 A. Because an as-grown film does not indicate any XRD patterns from the material (figure 4.5.) annealing treatments were performed under N₂ to facilitate the formation of the crystalline structure. Although the N₂ treatment at 500 °C produces only a small amount of the crystal growth, annealing at 600 °C for 1 h significantly improved the crystallinity of the film (Figure 4.6.). Further treatment for 2 h did not improve the crystallinity, and thus, 1 h of treatment was chosen thereafter.
Figure 4.5. XRD of SnWO$_4$-(180) and SnWO$_4$-(350) thin films annealing at different temperatures for varied times under nitrogen.

The (002), (111), (121), and (040) peaks were indexed according to the JCPDS 29-1354. The crystallization increases with an increased film thickness. In this particular system, the (121) plane is usually the most prominent peak,$^{29,30}$ but in film growth, a preferential
crystal orientation with the (0k0) plane was observed. SnWO$_4$-(350) shows a small presence of a SnW$_3$O$_9$ new phase, as denoted by an asterisk in Figure 4.6. (A).

![Figure 4.6](image)

Figure 4.6. A) The XRD patterns of the $\alpha$-SnWO$_4$ thin films and (b) DFT-optimized crystal structure of $\alpha$-SnWO$_4$. The blue, gray, and red atoms denote Sn, W, and O, respectively. The rigid frameworks highlighted in the structure represent the SnO$_4$ tetrahedral and the WO$_6$ octahedral species. Asterisk denotes the SnW$_3$O$_9$.

Surface morphology observed by scanning electron microscopy (SEM) can confirm the polycrystalline character and the formation of grains in the SnWO$_4$ films. Figure 4.8 shows that the as-grown film (SnWO$_4$-(350)) has dense smooth growth of the film. After thermal annealing in Figure 4.7. B, a gradual increase in the size of nano-grains was observed leading to an increase of the sample surface roughness of the films. Also as in Figure 4.7.B, SnWO$_4$-(180) shows the co-existence of several orientations relative to the surface topology. For SnWO$_4$-(350) in Figure 4.7.D, there is more agglomeration of the
grains due to the crystallization increase. Hence, annealing caused some grain formation and produced rougher surfaces in all films compared to the as grown film. Those observations are in a good agreement with the XRD results.

Figure 4.7. The SEM images of SnWO$_4$ films, (a) as-grown SnWO$_4$-(350) thin film, (b) SnWO$_4$-(80), (c) SnWO$_4$-(180) and (d) SnWO$_4$-(350).

First-principles calculations based on DFT and DFPT within the HSE06 functional were carried out on the optoelectronic properties of α-SnWO$_4$ to obtain insight into the photocatalytic performance of this material. The DFT-optimized unit cell designed for this material is presented in Figure 4.8. B. The crystal lattice of α-SnWO$_4$ is orthorhombic (space group $Pnma$) and composed of two-dimensional (2D) sheets of distorted WO$_6$ octahedra, separated by layers of Sn$^{2+}$ ions, which are four-fold coordinated by O. Three distinct W-O bond lengths ($2 \times 1.802$, $2 \times 1.889$, $2 \times 2.141$ Å) and three different Sn-O bonds ($2 \times 2.184$, $2 \times 2.392$, $2 \times 2.826$ Å) were obtained from the DFT-optimized structure.
The calculated lattice parameters \((a = 5.592 \, \text{Å}, \, b = 11.632 \, \text{Å}, \, c = 4.983 \, \text{Å}, \, \alpha = \beta = \gamma = 90^\circ)\) are found to be in excellent agreement with the measured XRD data.

Figure 4.8. Calculated electronic density of states (DOS) and k-space band structure diagram of \(\alpha\)-SnWO\(_4\) using the DFT/HSE06 method. Color legend: total DOS in black, DOS projected on Sn in red, on W in blue and on O in green. The top of the valence band \(E_{VB}\) is represented by the horizontal dotted line. Fermi level is set at 0 eV.

The computed electronic density of states (DOS) and energy dispersion diagram that were produced using the DFT/HSE06 method are shown in Figure 4.8. The valence band states that are located within the 0-1.5 eV range below the Fermi level are dominated by a strong mixing of fully filled Sn 5s and O 2p orbitals. The conduction band states are mainly composed of empty W 5d orbitals. The calculations predict this material to be an indirect-type (\(\Gamma-X\)) semiconductor with a lowest-energy band gap of 1.52 eV that originates from
the Sn 5s$^2 + O 2p^6 \rightarrow W 5d^0$ orbital transitions. Note that no spin-orbit coupling effect was found in the electronic structure of this compound.

The transmittance spectra of the films deposited on FG substrates are shown in Figure 4.9. a. The film depicts a continuous decrease of the transmittance towards higher wavelengths with increasing film thickness, as expected from the Beer-Lambert law. Also, typical fringes resulting from interferences between the air/film and film/substrate interfaces were observed. Their oscillations amplitude and width depends on the thickness and the refractive index of the film. These oscillations increase with the film thickness assuming that the films have the same phase. To gain more rigorous calculation, the films reflectance was measured by taking reflectance into account, and the results are presented in Fig 4.9.b. The difference in oscillations observed in reflectance is also due to the same interferences phenomena in the film interfaces. An average reflectance around 15% was observed.

Figure 4.9. (A) Transmittance and (B) reflectance spectra of (a) SnWO$_4$-(80), (b) SnWO$_4$-(180) and (c) SnWO$_4$-(350) thin films grown on FG substrate.
From both transmittance and reflectance contributions with accurately accounting for the films thicknesses, the absorption coefficient of the material is determined. For each sample, the absorption coefficient was extracted by using the following the Londenquai formalism:\textsuperscript{46}

\[
\alpha = \frac{-1}{t} \ln \left( \frac{T}{(1-R)^2} \right)
\]

where \(\alpha\) is absorption coefficient, \(t\) is film thickness, \(T\) is transmittance, and \(R\) is reflectance.

Figure 4.10. The absorption coefficient spectra of the SnWO\(_4\) that were measured with different thicknesses and calculated using the DFPT/HSE06 method.

The computed spectrum using the DFPT/HSE06 method is compared in Figure 4.11. to the experimental spectra. It reveals the appearance of high- intensity absorption features
 (> $4.5 \times 10^5 \text{ cm}^{-1}$) in the UV range and a lower-intensity absorption band (< $2 \times 10^5 \text{ cm}^{-1}$) in the visible range, with a broad edge extending up to 800 nm. The calculated absorption spectrum is in excellent agreement with the experimental data obtained for SnWO$_4$-80 and SnWO$_4$-180 samples, while SnWO$_4$-350 shows a different behavior in the 650–800 nm. This is probably due to the presence of secondary phase with lower absorption coefficient. The weak edge absorption in the visible region suggests that the measured absorption coefficient (see Tauc plots for direct and indirect band gaps; Figure 4.11.) is consistent with its calculated indirect band gap (Figure 4.11.).

Figure 4.11. Tauc plots of (A) direct and (B) indirect bandgap of the SnWO$_4$-(180) thin films.

4.2.3. Charge separation and dielectric properties.

In previous experimental studies on common semiconductors used in photovoltaic devices, it has been demonstrated that a value of 10 or more for the optical dielectric constant is quite enough to obtain a good exciton dissociation into free charge carriers. $^{17,47-48}$ Moreover, it has been shown that the charge carrier effective masses must be smaller than
$0.5m_0$ ($m_0$ is the free electron mass) to obtain a good mobility.\cite{47} On the basis of these two conditions, the exciton dissociation and the charge carrier transport properties of $\alpha$-SnWO$_4$ were discussed and evaluated.

Furthermore, knowing the dielectric constant, the donor density of the material can be calculated. This is an important parameter to describe the semiconductor intrinsic nature. To estimate the dielectric constant, the complex index of refraction $N = n + ik$ was measured. From the fringes observed in the transmittance and reflectance spectra (Figure 4.12. a and 4.12. b), the refractive index $n$ can be calculated. Furthermore, knowing the absorption coefficient, the absorption index $k$ (or absorptance) is deduced:\cite{49}

$$n = \frac{f(\lambda_1,\lambda_2)}{2(\lambda_1 - \lambda_2)t} \quad (4.2)$$

Where $f$ is the fringe number, $\lambda_1$ is the maximum wavelength, $\lambda_2$ is the minimum wavelength and $t$ is the film thickness.

The absorption index is equal to $k = \frac{\alpha \lambda}{4\pi}$, where $\alpha$ is the absorption coefficient. In the spectral range of 600-2000 nm, $n$ was found to be 2.5 and 2.68 for SnWO$_4$-(180) and SnWO$_4$-(350); respectively. Correlating the complex index to the dielectric properties then becomes:

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = N^2 = (n + ik)^2 \quad (4.3)$$

The dielectric constant can be deduced by $\varepsilon_1 = n^2 - k^2 \approx n^2$ (for low absorption). Thus, the obtained dielectric constants were 6.25 and 7.2 in the visible spectral range for SnWO$_4$-(180) and SnWO$_4$-(350); respectively.
The dielectric constant and electron effective mass determination of SnWO$_4$-(80) thin films.

Because of the very thin thickness of SnWO$_4$-(80) sample, there were no fringes observed. Hence, another formalism was used to extract dielectric constant. The dielectric constant is deduced from a calculation of real part of index of refraction coming from reflectance and transmittance measurements.\textsuperscript{50}

\[
n = \frac{(1 + R)}{(1 - R)} + \sqrt{\left(\frac{4R}{(1 - R)^2}\right)} - k^2
\]  

(4.4)

The real part of the dielectric constant $\varepsilon_1$ is related to the wavelength $\lambda$ in the non-absorbing region by the following equation \textsuperscript{51,52}

\[
\varepsilon_1 = \varepsilon_r - \frac{e^2N_p}{4\pi\varepsilon_0m\lambda^2}
\]

(4.5)
Where $e$ is the electron charge, $\varepsilon_0$ is the permittivity of free space, $c$ is the velocity of light $N_D$ is the donor density and $m^*$ is the effective mass.

Figure 4.12 shows the plot of $\varepsilon_1$ vs. $\lambda^2$ for the SnWO$_4$-(80) thin films. The intersection of the linear part of this curve gives the value of $\varepsilon_L$ and the ratio $N_D/m^*$ can be calculated from the slope of the straight line. The MS plots only depict the potential window in which the faradic current remains negligible in accordance with the cyclic voltammetry (CV). The flat band potential of the films was obtained by extrapolation to the X-axis of the MS (C–2 against potential), and the majority charge carrier concentration ($N_D$) can be extracted from the slope of the linear fit according to the following equation 4.6:

$$\frac{1}{C^2} = \frac{2}{eA^2\varepsilon_\varepsilon_0N_D} \left( E_{app} - E_{FB} - \frac{k_BT}{e} \right)$$

(4.16)

From the intercept of Figure 4.12, dielectric constant was found to be equal to 7.6 which was used to estimate the effective mass of the material. Indeed, effective mass is another

![Figure 4.13](image-url)

Figure 4.13. The (A) CV and (B) MS measurements of SnWO$_4$-(80) thin film.
important parameter that can give an idea about the charge diffusion in the photocatalyst. This parameter was never been reported for tin tungstate based material. Acceptable effective mass must be less than 0.5 for an efficient charge carrier’s diffusion in the material.\(^{47}\) For a measured donor density of \(1.8 \times 10^{20}\) cm\(^{-3}\); deduced from CV and MS measurements (Figure 4.13.), the electron effective mass at \(m_e^* = 0.47\) \(m_0\) for SnWO\(_4\) - (80) was estimated. All the extracted dielectric constant and effective mass values are assembled in Table 4.1 with the corresponding calculated values. They will be discussed in correlation with PEC performances.

Table 4.1. Calculated high-frequency (\(\varepsilon_\infty\)) dielectric constants and effective masses of holes (\(m_h^*\)) and electrons (\(m_e^*\)) in the three principal directions of \(\alpha\)-SnWO\(_4\) using the DFT/HSE06 method. The calculated values are compared to the current experimental data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dielectric Constant ((\varepsilon_\infty))</th>
<th>Effective Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>DFT/HSE06</td>
</tr>
<tr>
<td></td>
<td>DFT</td>
<td></td>
</tr>
<tr>
<td>(\alpha)-SnWO(_4)</td>
<td>SnWO(_4)-(80): 7.6</td>
<td>6.2 [100]</td>
</tr>
<tr>
<td></td>
<td>7.1 [010]</td>
<td>106.5 [010]</td>
</tr>
<tr>
<td></td>
<td>6.3 [001]</td>
<td>31.8 [001]</td>
</tr>
<tr>
<td></td>
<td>6.5 (Average)</td>
<td>55.8</td>
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<td>(average)</td>
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</table>

The electronic contribution (\(\varepsilon_{\infty}\)) to the dielectric constants was also calculated using the DFT/HSE06 method, and the values are 6.2, 7.1, and 6.3 along the [100], [010], and [001] directions, respectively (see Table 4.1.). The calculated average value (arithmetic mean) of
6.5 is in the same order of the experimental value. The ionic contribution ($\varepsilon_{vib}$) to the dielectric constant was also computed using the DFPT/Perdew-Burke-Emzerhof exchange-correlation functional (PBE) method, and much larger values of 29.1, 106.5, and 31.8 were obtained in the three principal directions with an average value of 55.8 (see Table 4.1.). This leads to a static dielectric constant of 62.3. The major contribution of the static dielectric constant that is due to the ionic portion originates from the strong ionic character of the crystal. The effective masses of the photogenerated holes ($m^*_h$) and electrons ($m^*_e$) were also computed at the band edges using the finite difference method based on the band structure for $\alpha$-SnWO$_4$ in the three principal crystallographic directions. The results obtained (Table 4.1) show that both holes and electrons have large effective masses along some directions, e.g., ($m^*_h$) = 1.76 m$_0$ and ($m^*_e$) = 1.23 m$_0$ along the [010] direction.

Figure 4.14. The (A) photoelectrochemical activity of (a) SnWO$_4$-(80), (b) SnWO$_4$-(180) and (c) SnWO$_4$-(350) thin films and the (B) stability of SnWO$_4$-(80) photoanode.

The Figure 4.14. presents the photoelectrochemical (PEC) measurements of the $\alpha$-SnWO$_4$ thin films. The cathodic scan was used and it was chosen to start at 0.3 V vs. RHE to avoid any surface Sn$^{2+}$ redox reactions. All of the films are photoresponsive under solar AM 1.5
G illumination. In terms of the photocurrent density, 40, 25, and 16 μA cm$^{-2}$ have been measured for SnWO$_4$-(80), SnWO$_4$-(180), and SnWO$_4$-(350), respectively. The thinner film exhibits the highest photoactivity. As illustrated in Figure 4.14.B the photocurrent density of SnWO$_4$-(80) decreased after just one scan. It is known that Sn$^{2+}$ easily oxides into Sn$^{4+}$ and acts as a possible trap site of the electron.$^{53,54}$ The PEC performances for the SnWO$_4$-(350) in Na$_2$SO$_4$ aqueous solution adjusted with H$_2$SO$_4$ to pH 3 and with NaOH to pH 13 are also shown in Figure 4.15. The high improvement of the photocurrent with pH 13 compared to pH 3 can be noticed. Unfortunately, the material is not stable at this pH and the material dissolves after several scans. At this stage, the photocurrent is assigned to originate from material oxidation, likely Sn$^{2+}$ to Sn$^{4+}$.

Figure 4.15. The photoelectrochemical activity of (a) SnWO$_4$-(80) in solution of pH 3 and 13.
A protection layer, such as TiO$_2$, is essential to stabilize the PEC performance for future study. The measured photocurrent densities were still very low compared to other visible active photoanodes, but for the flat band potential determined by the Mott-Schottky measurements (Figure 4.12.), an interesting potential of $-0.14$ V vs. RHE was obtained which suggested that the photoanode has potential for the non-biased water splitting reaction.

As mentioned previously, the PEC performances are greatly influenced by the photophysical properties. Below, the absorption, dielectric constant (associated with charge separation), and effective mass (associated with charge transport) are separately. First, for the absorption coefficient, it was measured $4 \times 10^4$ cm$^{-1}$ at 600 nm. Thus, it requires 250 nm film thicknesses to sufficiently absorb the light irradiation in this wavelength range, which cannot explain the highest PEC performance of the thinnest material. Second, regarding the static dielectric constant, in previous experimental studies on common semiconductors, it has been demonstrated that a value of 10 or more is effective for exciton dissociation into free charge carriers. An electronic contribution of 7.6 (the calculated one is 6.5) was measured and calculated a value of 55.8 for the ionic contribution, which gives 62.3 for the static dielectric constant. Because this value is much higher than 10, this may indicate that $\alpha$-SnWO$_4$ has excellent dielectric properties that should reflect an efficient exciton dissociation. Finally, regarding the charge carrier effective masses, it has been shown that values smaller than 0.5 m$_0$ are needed to obtain an effective mobility. The measured electron effective mass of 0.47 m$_0$ for SnWO$_4$-80 is in good agreement with the average calculated value (geometric mean) of 0.35 m$_0$. The hole effective mass (average value) was predicted to be 0.8 m$_0$. Moreover, the DFT calculations
showed important anisotropies in both the hole and electron effective masses along the three principal orientations of the crystal, and there were much larger values than 0.5 m_0 in the [010] direction. Consequently, the presented calculations and experiments show that α-SnWO_4 exhibits a high probability of charge separation due to the anisotropic nature of the carrier effective masses, but it possesses low carrier mobility, which must be detrimental for the PEC activity. When the mobility is low, charge carriers can only travel for short distances. The high photocurrents observed with the thinner film may indicate that transport is the limiting factor. In addition to these aspects, the unstable oxidative character of Sn atoms in the α-SnWO_4 system leads to low and unstable PEC performance. Many strategies can be adopted to improve the transport properties, such as metal doping, nanostructuration to decrease the film thicknesses (improve transport), while preserving a high film absorption or via surface cocatalyst functionalization, but this is beyond the scope of this chapter.
4.3. Experimental and theoretical methods

4.3.1. Synthesis of powders

Stoichiometric molar quantities of SnO (Sigma Aldrich, 99.99%) and WO$_3$ (Sigma Aldrich, 95 %) were mixed homogenously by grinding for 20 min under an argon atmosphere, SnCl$_2$ (Aldrich, 99.99%) was added as a flux to provide a reactant to flux molar ratio of 1:10. The obtained mixture was ground again for 10 min under the argon atmosphere. The obtained mixture was transferred to a quartz tube and heated under vacuum for 2h at 800 °C. After 2 hours, rapid quenching from 670 or 800 °C for the β-SnWO$_4$ and radiative cooling for the α–SnWO$_4$.

4.3.2. Photoelectrodes

Sputtering deposition is generally used to grow films, with special care given to the thickness and morphology of the samples. According to the Thornton model sputtering,$^{41}$ dense, smooth and crystalline films are synthesized via processes at a low deposition pressure and a high substrate temperature, while rough and porous films are synthesized at a high pressure and a low substrate temperature. In this study, dense crystalline growth was chosen to maximize the charge transport for the reaction.

α-SnWO$_4$ films were grown by DC magnetron sputtering using W and SnO$_2$ targets. The deposition process was performed at room temperature on fused glass (FG) for the optical measurements and on fluorine doped tin oxide (FTO) substrates for the
photoelectrochemical measurements by adding O₂ reactive gas. The Ar and O₂ flows were held constant at 20 and 2 sccm, respectively. The total pressure was 1.33 Pa. The direct current (DC) power densities were set to 7.30 and 6.08 W cm⁻² for the SnO₂ and W targets, respectively. To facilitate the formation of the crystalline structure, annealing treatments were conducted under N₂ at 600 °C for 1 h. The structural characterization of the thin films was performed by recording conventional 0-2θ X-ray diffraction patterns from a Bruker Discover diffractometer (Cu Kα1 radiation) with a 0.01° step size and a 0.5 s counting time per step. The morphology observations were conducted using a Nova Nano630 Scanning Electronic Microscope (SEM) that was operated at 5 kV (the resolution is close to 3 nm). The transmittance and reflectance UV-visible spectra were obtained on films that were deposited on FG substrates. The spectra were recorded in the range of 200 to 2000 nm using a Jasco V-670 spectrophotometer with an integrating sphere. The thin film thicknesses were measured using a profilometer on a FG substrate that was masked with a tip.

### 4.3.3. Electrochemistry

All electrochemical and PEC procedures were performed using Milli-Q water (18 MΩ). Sodium sulfate (Na₂SO₄, ≥99.99%, Aldrich), sodium hydroxide (NaOH, 99.99%, Sigma-Aldrich), and sulfuric acid (H₂SO₄, 99.999%, Aldrich) were used as received to prepare the required electrolytes. All experiments were performed using a research-grade, multi-channel potentiostat (VMP3, BioLogic Science Instruments). A Pt wire and an Ag/AgCl (saturated KCl) electrode were used as the counter and reference electrodes, respectively.
All experiments were recorded against this reference electrode, which was calibrated against an RHE. The results were then reported on the RHE scale using:

\[
(V \text{ vs. RHE}) = (V \text{ vs. Ag/AgCl}) + 0.197 + 0.0591 \times \text{pH}
\]  

(4.7)

The CV experiments were performed using a regular one-compartment electrochemical cell with a three-electrode configuration. The PEC measurements were conducted using a 3-electrode system and a potentiostat (Biologic, VMP3). The SnWO₄ electrode was used as the working electrode, the silver/silver chloride (Ag/AgCl) electrode (saturated in sodium chloride (KCl) aqueous solution) was used as the reference electrode, and a platinum wire was used as the counter electrode. A solar simulator (Peccell Technologies, PEC-L15) was used to illuminate the air mass 1.5 global (AM 1.5 G) simulating spectra. An anodic sweep was conducted at 10 mV s⁻¹.

### 4.3.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy was performed to estimate the flat band potential and the flat band position of the prepared SnWO₄ films. The same conventional three-electrode was used in a single electrochemical cell. The electrochemical impedance spectroscopic investigations were performed in a 0.2 M Na₂SO₄ solution that was adjusted with H₂SO₄ at a pH of 3. For the measurements, potentiostat system (VMP3) from BioLogic Science Instruments was used. To determine the potential window for the Mott-Schottky analysis, cyclic voltammetry experiments were conducted a scan rate of 10 mV s⁻¹ between 0.8 and 1.3 V vs. RHE under bubbling Ar. The impedance spectra were recorded between 10 to 100 kHz under bubbling Ar, and the amplitude of the superimposed
sinusoidal potential signal was 5 mV for each of the 70 steps in the potential window starting from 1.3 to 0.8 V vs. RHE in dark conditions.

### 4.3.5. Theoretical models

The electronic structure of α-SnWO₄ was calculated using DFT by employing the range-separated hybrid HSE06 exchange-correlation functional, as implemented in the VASP program. The crystal structure of this material was fully optimized with the PBE functional. The Brillouin zone was sampled with a 5 × 3 × 5 Monkhorst–Pack k-point grid. Gaussian smearing was used for the energy dispersion curves, while the Brillouin zone integration was performed with the tetrahedron method with Blöchl corrections.

The UV-Vis absorption properties of the α-SnWO₄ were calculated in the framework of the density functional perturbation theory (DFPT) implemented in VASP using the HSE06 functional. The optical absorption coefficient (α(ω) in cm⁻¹) was obtained using the equation

\[
\alpha(\omega) = \frac{4\pi k(\omega)}{\lambda}.
\]

The λ and ω are the wavelength and the frequency of the incident light, respectively. k(ω) is the extinction coefficient that is defined by

\[
k(\omega) = \left(\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1}{2}\right)^{\frac{1}{2}}.
\]

Finally, ε₁(ω) and ε₂(ω) represent the real and imaginary parts of the frequency-dependent complex dielectric function, respectively.

The optical or electronic contribution (εᵥ) to the static dielectric constant tensor of the α-SnWO₄ was computed using the optical or electronic contribution (εᵥ) to the static dielectric constant tensor of the α-SnWO₄ was computed using the self-consistent response of the crystal to a finite electric field that was implemented in VASP by
employing the HSE06 functional. The vibrational contribution tensor ($\varepsilon_{\text{vib}}$) was obtained by computing the full phonon spectrum of the crystal using DFPT within the linear response method that is implemented in VASP and the PBE functional.

The effective mass tensors of the photogenerated holes ($m_h^*$) and electrons ($m_e^*$) at the band edges of the $\alpha$-SnWO$_4$ were computed using the finite difference method$^{66}$ and by considering the $k$-space band structure that was obtained from HSE06.

4.4. Summary

In summary, a combined experimental and theoretical approach was used to determine the photophysical properties of $\alpha$-SnWO$_4$, including the band gap, absorption coefficient, dielectric constant, and charge carrier effective masses. All of the measured and calculated properties are in excellent agreement.

Thin films of various thicknesses were deposited on FG and FTO substrate by reactive DC magnetron sputtering by simultaneous deposition of W and SnO$_2$. XRD measurements realized on the samples showed that thickness increase the films crystallization and orientation. The absorbance, determined by the contribution of transmittance and reflectance spectroscopy, were also increased with the film thickness. The films can absorb more than $2 \times 10^5$ cm$^{-1}$ at 400 nm and $4 \times 10^4$ cm$^{-1}$ at 600 nm. This absorption coefficient shows that 250 nm of film thickness is more than enough to catch all the irradiated photon until 600 nm wavelength. Despite the fact that SnWO$_4$ present interesting absorbance properties, and efficient charge carriers extraction (dielectric constant more than 30), it suffers from weak diffusion properties that reduce PEC response reflected by a high
effective masses especially in the (010) direction (more than 1.23 m₀) which is one of the
dominant orientation in the films. In addition to those parameters, the surface state of α-
SnWO₄ may presents a concentration of inactive sites for water oxidation (Sn⁴⁺) that can
explain also the low PEC responses. Thin films photophysical experimental
characterizations and theoretical calculations constitute an excellent tool for better
understanding and improvement of photocatalyst PEC efficiency. The methodology
presented in this study provides an excellent tool to deeply understand the
photoelectrochemical performance of various materials at high accuracy.³⁶
4.5. References

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CHAPTER 5

Hydrothermal synthesis of Sn$^{2+}$ pyrochlore-Type antimonates: Understanding the role of Sn$^{2+}$ in the crystal structure

5.1. Introduction

One of the main challenges that limit synthesis of Sn$^{2+}$-based material is their instability under high-temperature at which conventional solid state synthesis commonly operates. Under these harsh conditions, the Sn$^{2+}$ tends to disproportionate to form metallic Sn and Sn$^{4+}$ species. Despite this difficulty, Sn$^{2+}$-containing oxide materials have attracted attentions because of their interesting electronic structures, low cost, high abundance and suitable band gaps for visible responsive photocatalysis. The main advantage of Sn$^{2+}$-containing oxides for photocatalytic application is visible-light absorption because of the presence of lone pair electrons from their $s^2d^{10}$ electronic configuration, similar to those of the toxic Pb$^{2+}$-containing oxide materials. Hence, Sn$^{2+}$-based compounds are classified to environmentally benign materials compared to Pb$^{2+}$-based compounds. Sn$^{2+}$ oxides mixed with d$^0$ transition metals such as W$^{6+}$, Nb$^{5+}$, Ta$^{5+}$, and Ti$^{4+}$ were reported.$^1$-$^4$

The pyrochlore crystal structure in particular is an interesting structure because of its versatile nature. In the ideal structure, it is represented by $A_2B_2O_7$ stoichiometry, where $A$ is a fairly electropositive cation and $B$ cation forms $BO_6$ octahedra; however, it is known to be defective with $A$ cation, thus forming oxygen vacancies.$^5$-$^6$ It is reported that the presence of main group cation at the $B$ site such as Sn or Sb creates a favorable electronic interaction between the $B5s$ and $O2p$ orbitals.$^7$ Therefore, it is interesting to study
coordination of Sn\(^{2+}\) as an A cation in a pyrochlore structure with antimony as a B cation. However, considering tin antimony based structure, the synthesis method is challenging because Sb\(^{5+}\) may be reduced into Sb\(^{3+}\) forming Sb\(_2\)O\(_3\) as a favorable product at high temperatures. For synthesis of the Sn and Sb mixed oxides, the main product is known to form Sn\(_{1-x}\)Sb\(_x\)O\(_2\).\(^8\)\(^9\) Therefore, soft methods which can operate at low temperatures such as ion exchange, solvothermal or hydrothermal synthesis are more suitable. So far, the attempts to synthesize Sn\(^{2+}\) and Sb\(^{5+}\) containing pyrochlore structure was achieved through ion exchange method of antimonic acid precursor at room temperature,\(^10\) or at different temperatures (30, 60, and 90 °C).\(^11\) In this regard, the pyrochlore antimonic acid is a very good candidate as it has been studied extensively as an ion exchanger in nuclear wastewater treatment applications.\(^12\) This is due to their excellent ion-exchange capabilities toward several alkali and alkaline earth metal ions (Na\(^+\), Rb\(^+\), Cs\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\))\(^13\)\(^-\)\(^14\) and transition metal ions (Co\(^{2+}\), Mn\(^{2+}\), Ni\(^{2+}\)).\(^15\)\(^-\)\(^17\) In addition silver ion exchanged pyrochlore oxides were prepared by the reaction of antimonic acid and silver nitrate solution at room temperature.\(^18\)\(^,\)\(^19\)

Nonetheless, the stoichiometry of the material and the position of Sn\(^{2+}\) in the Sn\(_x\)Sb\(_y\)O\(_z\) crystal structure has not been clarified. Furthermore, the effect of local coordination of Sn\(^{2+}\) into the electronic structure and the consequent optoelectronic properties need to be studied. In this chapter, the hydrothermal synthesis of Sn\(^{2+}\) antimonate pyrochlore material is discussed. The hydrothermal synthesis gives control on the quantity of Sn\(^{2+}\) into the pyrochlore antimonic acid structure through modifying reaction temperature, duration, pH, and solvent. The crystal structure of the obtained products was studied by XRD and analyzed by Rietveld refinement. The amount of tin present in the compound was
quantified using inductively coupled plasma (ICP). The size, morphology and structure of
the obtained material were studied by SEM and high resolution transmission electron
microscopy (HRTEM) with selected area electron diffraction (SAED). The elemental
mapping was done to probe the positions of tin and antimony into the structure. The
absorption properties were studied by diffuse reflectance (DR) UV-Vis spectra and the
Corresponding emissions by photoluminescence (PL). The intrinsic flat band potential of
the material was measured through Mott-Schottky analysis. The photoelectrochemical
measurements were performed for oxygen evolution.

5.2. Results and Discussion

5.2.1. The Crystal structure

Figure 5.1. shows the calculated, experimental, and difference X-ray diffraction pattern for
the H₂Sb₂O₆.nH₂O (antimonic acid) synthesized by hydrothermal method. The vertical
lines below the profiles mark the position of all possible Bragg reflections.
Figure 5.1. The calculated, experimental, and difference X-ray diffraction profiles for the H$_2$Sb$_2$O$_6$.nH$_2$O (antimonic acid) synthesized by hydrothermal method.

The XRD pattern shows a pure phase material of the H$_2$Sb$_2$O$_6$.nH$_2$O material assigned to (JCPDS No. 01-084-0303) with a cubic crystal structure belonging to the Fd3m space group. Since the crystal structure of antimonic acid is known to be affected by the synthesis method and the degree of hydration, Rietveld refinement was performed to deduce the stoichiometry. The atom positions, occupancy, and the number of atoms from the analysis are summarized in Table 5.1.
Table 5.1. The atom sites positions, occupancy, and number of atoms from Rietveld refinement of the antimonic acid sample.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occupancy</th>
<th>Number of atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb (5+)</td>
<td>16</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>O</td>
<td>48</td>
<td>0.31813</td>
<td>0.12500</td>
<td>0.12500</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>O’</td>
<td>32</td>
<td>0.44413</td>
<td>0.44413</td>
<td>0.44413</td>
<td>0.44</td>
<td>1.92</td>
</tr>
</tbody>
</table>

Based on literature, the most accepted structure for antimonic acid is the one in which Sb and O (1) atoms, consisting of the three dimensional corner shared SbO₆ octahedra (as shown in Figure 5.2.) are placed on 16c (0, x, x) and 48f site (x, 1/8, 1/8) respectively.²⁰,²¹,²² In addition, Slade et al. have revealed by neutron powder diffraction refinement that the O(2) atoms of the H₂O or H₃O⁺ species are correctly positioned on a 32e site (x, x, x).²¹ Having this in mind, the data were refined where Sb (0, 0.02846, 0.02846), O1 (0.33900, 1/8, 1/8), and O’ (0.54, 0.54, 0.54). The stoichiometry was deduced to be H₂Sb₂O₆.1.76H₂O.
Figure 5.2. The crystal structure of antimonic acid, brown octahedra represent the $(\text{SbO}_6)$ and the red are the oxygens.

The quantitative measurement of tin amount in the bulk of samples was conducted by ICP and the results are expressed as Sn/Sb molar ratio. Table 5.2 shows a summary of the reaction conditions and ICP molar ratio.

For the samples synthesized at 60 °C, increasing the time from 6 to 12 h increased the Sn/Sb ratio from 0.61 to 0.85 but increasing the time further to 24 h did not increase the amount of Sn. Similar behavior was observed for the sample synthesized at 90 °C where Sn:Sb ratio reached 0.96 at 12 h and did not increase further at 24 h. The Sn/Sb ratio increased from 0.36 at 30 °C (SnSb-30-12h) to 0.59 at 45 °C (SnSb-45-12h) and reached the maximum of 0.98 at 90 °C (SnSb-90-12h). Beyond this temperature the ratio reaches 1.36 at 120 °C synthesis, which is greater than the theoretical starting ratio, indicating that the antimonic acid was probably decomposed and the Sb amount was decreased.
Powder XRD patterns were used to analyze the crystal structure of the obtained powders knowing the ICP results. Table 5.2 shows summary of the reaction conditions and ICP molar ratio:

Table 5.2 Summary of the reaction conditions and ICP

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sn/Sb (molar ratio)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnSb-30-12</td>
<td>0.36</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>SnSb-45-12</td>
<td>0.59</td>
<td>45</td>
<td>12</td>
</tr>
<tr>
<td>SnSb-60-6</td>
<td>0.61</td>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>SnSb-60-12</td>
<td>0.85</td>
<td>60</td>
<td>12</td>
</tr>
<tr>
<td>SnSb-60-24</td>
<td>0.86</td>
<td>60</td>
<td>24</td>
</tr>
<tr>
<td>SnSb-90-12</td>
<td>0.96</td>
<td>90</td>
<td>12</td>
</tr>
<tr>
<td>SnSb-90-24</td>
<td>0.98</td>
<td>90</td>
<td>24</td>
</tr>
<tr>
<td>SnSb-120-24</td>
<td>1.36</td>
<td>120</td>
<td>24</td>
</tr>
</tbody>
</table>

Figure 5.3 shows the XRD patterns of the samples with tin incorporation named as SnSb-reaction temperature-time at different temperatures for A) 6 and 12 h between 30 and 90 °C; B) 24 h between 60 and 180 °C; and antimonic acid for comparison.

The main difference in the XRD pattern between obtained materials and the antimonic acid starting material was the decrease in the intensity of the all-odd (h, k, l) planes and a slight
shift of the 2θ into the higher angles, such as (111), (311), (113) (Figure 5.3. A). With increasing the synthesis temperatures from 30 to 60°C, the relative intensities for (311) and (222) progressively decreased from the antimonic acid precursor. At higher temperature at 90 °C, the relative intensity of (311) peak with respect to the (222) plane no longer changed, which may indicate the complete formation of a given bulk structure, likely suggesting the maximum tin incorporation of Sn^{2+} into the crystal structures. Increasing the reaction time for 24 h did not change neither the relative intensity nor the Sn:Sb molar ratio. However increasing the temperature higher than 120 °C, the characteristic peaks for SnO and SnO_2 and Sb_2O_3 started to appear and major phase of SnO was observed at 180 °C for 24 h. Therefore, the synthesis condition was set at 90 °C for 12 h hereafter. To understand the position of Sn^{2+} inside the crystal structure, sample SnSb-90-12 h with a maximum incorporation of Sn^{2+} was refined by Rietveld analysis.

Figure 5.3. The XRD patterns of the samples with tin incorporation named as SnSb-
reaction temperature-time at different temperatures for A) 6 and 12 h between 30 and 90 °C; SnSb-30-12, SnSb-45-12, SnSb-60-6, SnSb-60-12, SnSb-90-12 and B) for 24 h

Figure 5.4. The calculated (red), experimental (blue), and difference X-ray diffraction profiles (grey) for the SnSb-90-12 synthesized by hydrothermal method at 90°C for 12 h.

Figure 5.4 shows the XRD patterns of the SnSb-90-12 sample, the calculated one by Rietveld refinement and the difference curve. Refining this structure showed different atomic sites compared to the antimonic acid. Table 5.2 shows the summary of the atom site positions, occupancy, and the number of atoms. Keeping the Sb$^{5+}$ at the 16 c site and O at the 48 f position with a slight distortion of the x position from 0.33900 in the acid precursor to 0.32221 in the SnSb-90-12h. Most importantly, the Sn$^{2+}$ occupies the 16 d site (0.5, 0.5, 0.5) which is an interstitial site in the cavity of the for the pyrochlore-type antimonic acid. Due to the rigidity of the pyrochlore structure, the XRD pattern is not significantly
The decrease in the intensity of the planes and incorporation of Sn is confirmed by TEM as will be discussed later.

Table 5.3. The atom sites positions, occupancy, and number of atoms from Rietveld refinement of the SnSb-90-12.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>Number of atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(^{2+})</td>
<td>16</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.54</td>
<td>8</td>
</tr>
<tr>
<td>Sb(^{5+})</td>
<td>16</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>1</td>
<td>16</td>
</tr>
<tr>
<td>O</td>
<td>48</td>
<td>0.32</td>
<td>0.125</td>
<td>0.125</td>
<td>1</td>
<td>47</td>
</tr>
</tbody>
</table>
5.2.2. Morpological analysis

The morphology and the textural properties of these materials were studied by SEM (Figure 5.5) and HRTEM (Figures 5.6, 5.7). It is clear that samples with low tin content preserved the starting octahedral structure of the starting material affording regular and well defined octahedra. This is the case for SnSb-30-12 and SnSb-45-12 samples where the particle size was estimated around 100 nm. Increasing the tin content in the SnSb-60-12 sample (Sn/Sb=0.85) showed an aggregated morphology with destructions of the octahedral structure and the effect is clearer in the SnSb-90-12 sample (Sn/Sb=0.95).
HRTEM of the starting precursor (Figure 5.6 a) with lower magnification clearly showed the octahedral geometry and small nanoparticles of were also observed on the surface of large octahedra. The corresponding SAED shows as expected a well crystalline material. Figure 5.6. c shows a HRTEM image and the corresponding FFT. From the FFT, the diffraction pattern observed corresponds to typical cubic cell in the pyrochlore structure.

Figure 5.7 shows the (a) HRTEM of the SnSb-90-12 sample with the Sn/Sb=1 and (b) the corresponding FFT. It can be clearly seen from FFT that upon the incorporation of tin the crystallinity decreases. This may be explained by two hypothesis: 1) the degradation of the octahedral structure into smaller nanoparticles or 2) the presence of excess amorphous tin (tin oxide) which doesn’t show in XRD. EFTEM elemental mapping of the antimonic acid sample and SnSb-90-12 is shown in figures 5.8 and 5.9 respectively.
Figure 5.6. (a) HRTEM image of the antimonic acid precursor with low magnification and (b) the corresponding SAED, c) HRTEM image with higher magnification and corresponding FFT patterns.
Figure 5.7 (a) HRTEM of the SnSb-90-12 h sample and the corresponding FFT pattern.

Figure 5.8 shows the elemental mapping of the antimonic acid precursor which shows the homogenous distribution of antimony (red) and oxygen (green) throughout the sample. Similarly, figure 5.9 shows the EFTEM mapping for each single element and the overlayed map. No excess tin (blue) or antimony aggregates appeared into the map. It is worth noting that the darker region in the HRTEM reflect thicker areas which are reflected by dark blue color in the map. It is important to note that this does not represent the excess tin but is an artifact in the map and focusing should be on the single particles.
Figure 5.8. EFTEM mapping of the antimonic acid precursor (a) antimony map, b) oxygen map, c) the tin and antimony map and d) the corresponding TEM image.

Figure 5.9. HRTEM (a) and SAED (c) of the SnSb-90-12 sample and the corresponding EFTEM maps (b) antimony map (red), (d) the tin map (blue) f) oxygen map (green), e) the tin and antimony and oxygen map.
5.2.3. Absorption properties

The absorption properties of these materials were studied by DR.UV-Vis spectra. The photoluminescence study was conducted to understand the emissions of the material and to predict the plausible role of the electronic configuration of Sn$^{2+}$.

![Figure 5.10. a) The DR.UV-vis spectra of the tin antimonate samples with different temperature and time and b) the corresponding photoluminescence spectra.](image)

The absorption spectra (Figure 5.10 a) showed a significant band edge shift of the material from the UV region (400 nm) into almost 700 nm. This red shift is interesting if it comes from the intrinsic band gap. The trend in the shift of the band edge is parallel to tin amount. As discussed earlier, while keeping a pure phase XRD pattern, the maximum tin amount is reached in samples material of SnSb-90-12 and SnSb-60. It can be clearly seen that the absorption edge redshift increases in the order of SnSb-45-12 then at maximum tin amount have exactly the same band edge (SnSb-60-12 and SnSb-90-12), further increase in the tin...
creates a blue shift and increase in the background which is accompanied by the presence of SnO$_2$ peak into the structure. Therefore to understand the role of the local electronic environment, photoluminescence was performed (Figure 5.10b). In figure 5.10 B, based on the absorption spectra that were obtained, excitation around 520 nm will give a rise to a band-like emission. Interestingly, this feature was not present in the original antimonic acid sample and when the amount of tin was increased into the structure, the band width increased and became more defined. This confirms that the shift in the absorption is due to the presence of tin into the structure. However, the nature of Sn$^{2+}$ contribution into the electronic structure need to be studied further to explain whether it is contributing to valence band shift and therefore band gap narrowing or just creating defect states which result in narrowing of the band gap.

5.2.4. Mott-Schottky plot and photo-electrochemical activity

As explained earlier in chapter 1, one of the main thermodynamic requirements is the position of the band edges of the photocatalyst. Therefore Mott-Schottky analysis was performed for the SnSb-90-12 sample deposited on FTO by electrophoretic deposition (EPD). Figure 5.11 shows the Mott-Schottky plot of the film. From the positive slope of the curve, the material shows an n-type nature which is expected for the pyrochlore due to the presence of oxygen vacancies. As described earlier in detail, the intercept of the plot vs. x axis will give the flat band potential which can be estimated around 0.4 V vs. RHE suggesting that this material is not suitable for overall water splitting due to its positive conduction band edge. Therefore, this material may function as a PEC photoanode.
However so far, the photocurrent obtained is negligible (figure 5.12) and it mainly comes for Sn$^{2+}$ oxidation.

Figure 5.11 Mott-Schottky plot of SnSb-90-12 on FTO.

Figure 5.12. Photo electrochemical activity for hydrogen evolution of bare Sn$_x$Sb$_2$O$_6$ material (SnSb-90-12), in 0.5 M Na$_2$SO$_4$ solution adjusted with 1M H$_2$SO$_4$ to pH 0.2.
5.3. Experimental and characterizations

5.3.1. Synthesis of the antimonic acid precursor

The antimonic acid was prepared starting from 10 mmol of $\text{b}_2\text{O}_3$ (sigma Aldrich $> 99\%$) which was dissolved 60 ml of aqueous solution (30 $\%\text{H}_2\text{O}_2$, 20 ml) stirred for 1 h. then transferred into 100 ml autoclave and kept in oven at 90 $^\circ\text{C}$ for 12 h. The obtained powders are washed extensively with water and centrifuged several times. Then dried for 12 h at 60 $^\circ\text{C}$.

5.3.2. Synthesis of a series of tin antimonates

A series of tin (II)–antimonate materials with varied Sn content was prepared by modified hydrothermal synthesis. The preparation procedure was as follows: The as-prepared antimonic acid precursor ($0.25 \text{ g} \sim 2.5 \text{ mmol}$) was stirred in an acidified aqueous solution of $\text{SnCl}_2$ that was composed of concentrated HCl (0.5 g, 36 wt $\%$), $\text{SnCl}_2$ (5 mmol), and ultrapure water (30 mL) at room temperature for 1 h. Then the solution is transferred to Teflon autoclave and heated at several temperatures ($T= 30, 45, 60, 90, 120, 150, 180 \, ^\circ\text{C}$) for 6, 12, 24 h to facilitate the ion-exchange of $\text{Sn}^{2+}$ and $\text{H}^+$ ions. The resulting precipitate was then centrifuged, washed thoroughly with ultrapure water and EtOH, and finally dried in a vacuum drying oven at 60 $^\circ\text{C}$ for 12 h.

5.3.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded with a BRUKER D8 Advance diffractometer (DMAX 2500) using a Cu Kα energy source at 40 kV and 40 mA. Scanning
Electron Microscopy characterizations were performed on a Nova Nano 630 scanning electron microscope (SEM) from FEI company. The electron beam energy was set to 5 keV before the start of analysis. SEM measurements were used to determine the morphology as well as particle size of the synthesized particles. The SEM specimens were prepared by suspending them in ethanol and dispersing them by sonication. A drop of the solution was then poured onto the SEM stub and was dried before observations. The N\textsubscript{2} sorption studies were conducted using a Micrometrics ASAP 2420 to determine the Brunauer-Emmett-Teller (BET) surface area. The ICP measurements were performed using an ICP-OES Varian 72 ES. Digestion of the material was performed in the microwave digestion milestone of model ETHOS1. Diffuse reflectance spectra were measured using a UV-Vis spectrometer with an integrating sphere (JASCO, U-best 570) and were demonstrated according to the Kubelka-Munk function. Photoluminescence (PL) was measured using a Fluoromax-4 spectrofluorometer from Horiba Scientific. Transmission electron microscopy (TEM) analysis of samples was also performed to investigate the crystal structure, particle size and elemental composition present in the samples. The TEM analysis was carried out by setting the microscope in scanning TEM (STEM) and was accomplished by employing an aberration corrected Scanning TEM (STEM) microscope of model Titan G\textsuperscript{2} 60-300-ST from FEI Company. The microscope was operated at 300 keV beam energy during the STEM investigations and was the coefficient of spherical aberration of Condenser-2 lens was reduced to about 1 um to perform a high-resolution STEM analysis of the samples. The Fast-Fourier transform (FFT) analysis of the acquired micrographs were also calculated to measure the inter-planar d-
spacings of the crystalline phases present in the samples. The entire STEM analysis was performed in Gatan Microscopy Suite (GMS v. 1.83) software package from Gatan, Inc.

Elemental mapping was performed by using a post-column energy filter of model GIF Tridiem 863 from Gatan, Inc. The microscope was set to EFTEM mode to reduce the image magnification so that the field-of-view on the GIF CCD is about the same as that of the image-plane of the pre-GIF CCD.

### 5.3.4. Electrochemistry

All electrochemical and PEC procedures were performed using Milli-Q water (18 MΩ). Sodium sulfate (Na$_2$SO$_4$, ≥99.99%, Aldrich) and sulfuric acid (H$_2$SO$_4$, 99.999%, Aldrich) were used as received to prepare the required electrolytes. All experiments were performed using a research-grade, multi-channel potentiostat (VMP3, BioLogic Science Instruments). A Pt wire and an Ag/AgCl (saturated KCl) electrode were used as the counter and reference electrodes, respectively. All experiments were recorded against this reference electrode, which was calibrated against an RHE. The results were then reported on the RHE scale using:

$$(V \text{ vs. RHE}) = (V \text{ vs. Ag/AgCl}) + 0.197 + 0.0591 \times \text{pH} \quad (4.7)$$

The CV experiments were performed using a regular one-compartment electrochemical cell with a three-electrode configuration. The PEC measurements were conducted using a 3-electrode system and a potentiostat (Biologic, VMP3). The SnSb$_2$O$_6$ electrode was used as the working electrode, the silver/silver chloride (Ag/AgCl) electrode (saturated in sodium chloride (KCl) aqueous solution) was used as the reference electrode, and a
platinum wire was used as the counter electrode. A solar simulator (Peccell Technologies, PEC-L15) was used to illuminate the air mass 1.5 global (AM 1.5 G) simulating spectra. An anodic sweep was conducted at 10 mV s⁻¹.

5.3.5. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy was performed to estimate the flat band potential and the flat band position of the prepared SnSb₂O₆ films. The same conventional three-electrode single electrochemical cell was used. The electrochemical impedance spectroscopic investigations were performed in a 0.5 M Na₂SO₄ solution that was adjusted with H₂SO₄ at a pH of 0.23. For the measurements, a potentiostat system (VMP3) was used from Biologic Science Instruments. To determine the potential window for the Mott-Schottky analysis, cyclic voltammetry experiments were conducted a scan rate of 10 mV s⁻¹ between 0.8 and 1.3 V vs. RHE under bubbling Ar. The impedance spectra were recorded between 10 to 100 kHz under bubbling Ar, and the amplitude of the superimposed sinusoidal potential signal was 5 mV for each of the 70 steps in the potential window starting from 1.2 to 0.6 V vs. RHE in dark conditions.

5.4. Summary

A series of tin antimonate with pyrochlore structure was successfully synthesized using hydrothermal synthesis. This method offers control of the amount of tin into the structure which can be tuned by modifying the temperature and time. Rietveld refinement of the acid and the tin antimonate sample resulted in SnSb₂O₆ where tin occupies the interstitial
channels of the pyrochlore structure. The morphology change was identified by SEM and HRTEM; the octahedron morphology of the acid precursor is the dominant at low Sn loading whereas aggregates of small nanoparticles appears at high tin loading and destruction of the octahedral structure is noticed. These material showed interesting absorption edge with an extended absorption to 700 nm. Nonetheless, the role of Sn$^{2+}$ local electronic environment in this pyrochlore structure need to be understood by investigation of the electronic structure of the material for improved photocatalytic applications.
5.5. References

CHAPTER 6

Conclusions and outlook

Achieving efficient hydrogen production through photocatalytic overall water splitting relies mainly on the progress in development of visible-light-responsive photocatalysts. This challenge needs to be unraveled to achieve economically viable future fuel. The bulk of the semiconductor is the most crucial part of the photocatalyst as it is involved in the fundamental steps of photon absorption, charge separation, and charge carrier diffusion towards the surface. Although enormous advances have been achieved in the field of electrochemistry to understand the surface co-catalysts. Nonetheless, the bulk properties of the semiconductor and the complex competitive processes involved are poorly investigated. To achieve “photocatalysis by design”, the parameters that affect the fundamental processes need to be identified and improved. In particular, understanding the crystal and electronic structure is extremely important as these are the main factors that affect the aforementioned processes. In addition to that, improving the synthesis method utilized is crucial to enhance the efficiency of the photocatalyst. This dissertation focuses on a series of promising Sn$^{2+}$ and Bi$^{3+}$ metal oxides semiconductors. Two complementary approaches were followed to tackle the challenge; the first involves investigation of the detailed synthesis method. And the second is to perform a combined-experimental study of the optoelectronic properties of the photocatalyst.
In the beginning of the dissertation a series of bismuth titanate based material was studied; the pyrochlore (Bi$_2$Ti$_2$O$_7$ and non-stoichiometric Bi$_{1.75}$Ti$_2$O$_{6.62}$), the sillenite (Bi$_{12}$TiO$_{20}$) and the perovskite-like Bi$_4$Ti$_3$O$_{12}$. These materials show inconsistencies in their properties especially the bandgaps ranging between visible and UV responsive photocatalysts. To understand the intrinsic properties of these material, the bismuth titanate semiconductors were synthesized using co-precipitation synthesis method. The effect of the titanium to bismuth ratio was carefully studied.

For the pyrochlore family, a non-stoichiometric structure was obtained experimentally Bi$_{2-x}$Ti$_2$O$_{7-1.5x}$ instead of the stoichiometric Bi$_2$Ti$_2$O$_7$ and excess titanium was necessary to obtain single phase material. The titanium amount was optimized to 16% resulting in the Bi$_{1.75}$Ti$_2$O$_{6.62}$ structure which was confirmed by Rietveld refinement and ICP measurements. This clear distinction between the two structures was further supported by energy of formation calculations favoring a lower energy for the non-stoichiometric structure. Similarly the sillenite and perovskite-like powders were synthesized by the same methods and the Ti/Bi ratio was optimized to 12 and 0.75 respectively. Then using the optimized ratios, films of the non-stoichiometric structure were deposited using spin-coating technique of silicon substrate, fused glass, and fluorinated tin oxide. These films were utilized to perform and combined experimental-theoretical study determining the optoelectronic properties band gap, absorption coefficient, dielectric constant, and charge carrier effective masses. Large band gaps of 3.3 eV were experimentally which are in good agreement with the calculated 3.4 eV suggesting UV response. High dielectric constant was also obtained indicating excellent charge separation properties, however high electron
and holes effective masses in certain directions indicate a poor mobility of the carriers which may attributed to the vacancies.

The sillonite and the perovskite-like structures were found to be the UV responsive material, proving that the mistakenly reported narrow band gaps is due to the presence of secondary phases. From DFT calculations, the valence band is composed of Bi$^{3+}$ 6s$^2$ and O2p orbitals whereas the conduction band is composed of Ti 3d$^0$ for the pyrochlore and pervoskite-like structure and Bi$^{3+}$ 6p$^0$ orbital for the sillonite which afforded lower band gaps in comparison to the other two structures. High dielectric constants and low charge carrier effective masses were also predicted suggesting a good charge separation and transport properties. These material showed more negative flat band potential than the well-known TiO$_2$ opening the door to potential applications. This excellent agreement between the experimental and calculated values proves the accuracy of this approach and suggests these as an efficient tool to predict the properties of different photocatalysts. This approach is crucial as it leads to designing the photocatalyst by choosing the perfect of combination of elements as an alternative of the non-practical screening processes.

By understanding the contribution of bismuth in the electronic structure, the bismuth based compounds will in general exhibit large band gaps with exception to BiVO$_4$. Therefore the study was moved to investigate the Sn$^{2+}$ based compounds due to the contribution of the 5s$^2$ narrower band gap. The tin niobate SnNb$_2$O$_6$ structure was focused, which was previously reported to evolve either hydrogen or oxygen suggesting that it is a good candidate for overall water splitting. The main challenge for tin based compounds in general is the instability of Sn$^{2+}$ compounds and oxidation into Sn$^{4+}$ under high temperature synthesis methods which is detrimental for the photocatalytic activity. Therefore, the role
of flux assisted synthesis was investigated to control the properties of the tin niobate. The flux method provides control over the surface properties while maintaining high crystalline material with minimum defects. The XRD patterns and SEM analysis confirmed the formation of 2D platelets with increased anisotropic growth along bc plane as the flux to reactant ratio increased. The photocatalytic activity was improved as well as the flux to reactant ratio increased, which is explained by the beneficial role of synthesis of the flux in allowing the synthesis of tin niobate at a lower temperature compared to the solid state synthesis. The heightened activity is resultant coincided with the minimized amount of Sn$^{4+}$ on the surface and the plate like morphology which may be explained by minimized trap states. To understand the effect of plate like morphology on charge separation, a HRTEM and EFTEM study was performed to probe electrons and holes by photo deposition of metals and metal oxide however charge separation occurred in nm scale.

Next, the two approaches of synthesis and characterization on the SnWO$_4$ system were combined. Pure phase β-SnWO$_4$ was successfully synthesized using flux assisted method for the first time. The flux enabled the synthesis of pure phase material at even lower temperature than solid state synthesis. However, the study focused more on the optoelectronic properties of the α-SnWO$_4$ due to its interesting band gap. Discussing the nature of the band gap, 1.9 eV for a direct band gap and 1.7 eV for indirect band gap were obtained, consistent with the calculated indirect band gap of 1.52 eV. Based on the density of states calculation, the valence band top is composed Sn$^{2+}$ 5s$^2$ orbitals and O 2p$^6$ orbitals whereas the conduction band is dominated by W 3d$^0$ orbitals. High absorption coefficient was obtained extending to 800 nm. High dielectric constant and low effective masses were obtained at least in one direction. Although this material, has good charge separation and
charge transport properties, yet its photocatalytic and photoelectrochemical activity are limited by its oxidation under reaction conditions.

Finally, a study on Sn$^{2+}$ antimonate having pyrochlore structure was conducted to obtain visible-light-responsive material. Sn$^{2+}$ incorporation into H$_2$Sb$_2$O$_6$ base structure was achieved by hydrothermal method which provide control over the amount of tin by varying synthesis time and temperature. The main achievement of the study was identification of the exact position of tin in this new crystal structure using Rietveld refinement, confirming the SnSb$_2$O$_6$ stoichiometry leaving the lattice parameters of starting H$_2$Sb$_2$O$_7$ intact. An interesting absorption edge up to 700 nm was observed by incorporation of Sn$^{2+}$. Although photocatalytic activity of this synthesized material had low activity, there are margin of the study to be explored.

The study throughout this thesis elucidate a series of Sn$^{2+}$ and Bi$^{3+}$ based materials, explicating the promises but also challenges in synthesis and stability. There is tremendous opportunity using this type of oxides for photocatalytic application because of d$^{10}$s$^2$ electronic contribution of these elements, as clearly demonstrated in this thesis. Future works should be focused on protecting these tin based material by a passivating layer for example in order to get advantage of its good intrinsic properties.
LIST OF PUBLICATIONS

1. Flux-assisted synthesis of \( \text{SnNb}_2\text{O}_6 \) for tuning photocatalytic properties


2. The effect of temperature in flux-assisted synthesis of \( \text{SnNb}_2\text{O}_6 \)


3. Nano-design of quantum dot-based photocatalysts for hydrogen generation using advanced surface molecular chemistry


4. UV-Vis optoelectronic properties \( \alpha\text{-SnWO}_4 \): a comparative experimental and DFT study.


5. Combined Experimental-Theoretical Study of the Optoelectronic Properties of Non-Stoichiometric Pyrochlore Bismuth Titanate


6. Determination of the electronic, dielectric and optical properties of sillenite \( \text{Bi}_{12}\text{TiO}_{20} \) and perovskite-like \( \text{Bi}_4\text{Ti}_3\text{O}_{12} \) materials from hybrid first-principle calculations
Conferences


