Development of visible light active sodium tantalate photocatalyst for hydrogen generation

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Development of Visible Light Active Sodium Tantalate Photocatalyst for Hydrogen Generation

A thesis submitted to the Nanyang Technological University in fulfillment of the
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Abstract

Generation of hydrogen from water by using a photocatalyst and solar light is a clean and sustainable way to harvest energy. However the photocatalysts developed so far have limited efficiencies under visible radiation, due to lack of suitable photophysical properties. Band engineering of wide band gap photocatalysts is a promising approach to develop highly efficient, visible light driven materials. NaTaO_3 is one of the most efficient photocatalysts for the water splitting reaction under Ultra-Violet (UV) radiation. NaTaO_3 has large overpotentials and thus allows sufficient space for the modification of the band structure. Therefore, the objective of this project is to develop the visible light sensitive sodium tantalate based photocatalysts with suitable band edge potentials and band gaps. This work includes Density Functional Theory (DFT) based quantum chemical calculations on NaTaO_3 materials as well as synthesis, characterization and photocatalytic testing of the selected compounds. Firstly, using computation within the framework of DFT, the band structures of various doped NaTaO_3 systems were studied. The analysis of these results was carried out to identify the suitable dopants that would reduce the effective band gap of NaTaO_3 and enable the visible light absorption. Among the various candidates, Bismuth and Iron were selected as dopants. Experimental investigations were carried out on Bi doped NaTaO_3 and Fe and La-Fe co-doped NaTaO_3 powders. It was shown that in the case of Bi doping, the optical and photocatalytic properties of the powders can be changed significantly by tuning the synthesis conditions in the solid state synthesis. Bi doped NaTaO_3 powders prepared under mildly Na-rich conditions showed intense visible light absorption extending up to 550 nm. The samples prepared under these conditions were active photocatalysts for Methylene Blue

(MB) degradation and showed better performance than the commercially available catalysts (Degussa-P25) under the visible radiation ($\lambda > 420$ nm). These samples were also active for hydrogen evolution in presence of sacrificial agent under $\lambda > 390$ nm. The optimum conditions for hydrogen evolution (Bi content and amount of co-catalyst loading) were determined by controlled experiments carried out on series of samples. It was revealed that mildly Na-rich conditions led to approximately equal site occupancies of Bi ions at Na and Ta sites. Such occupancies result in the maximum band gap narrowing on account of Bi 6s induced mid-gap energy states as compared to the separate occupancies of Bi ions at Na and Ta site. Occupancy of Bi ions also maintains the ionic charge balance which is beneficial for the photocatalytic reactions. Bi doped NaTaO₃ powders were also prepared by low temperature hydrothermal method. These samples offered an advantage of larger surface area, however showed limited visible light absorption (up to 450 nm). Unlike the solid state synthesis, low temperature hydrothermal synthesis did not offer a control over site occupancies of Bi ions in the lattice. Nevertheless, the samples were active for hydrogen evolution under the visible radiation ($\lambda > 390$ nm) and the results were comparable with that of the solid state counterparts.

Visible light active Fe doped NaTaO₃, and La-Fe co-doped NaTaO₃ powders were prepared by the solid state route. Fe doped samples did not yield significant amount of hydrogen under the visible radiation which was attributed to the point defects in the lattice. On the other hand, La-Fe co-doped samples showed a maximum hydrogen evolution rate of 0.81 $\mu\text{moles}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ upon 0.05% Pt loading under the visible light radiation ($\lambda > 390$ nm). The structural characterization and detailed DFT calculations were carried out to understand the role of each dopant in the lattice. It was revealed that Fe ions enable the visible light

response, while La ions maintain the ionic charge balance in the lattice and creates characteristic surface nanosteps in co-doped NaTaO₃.

In conclusion, detailed computational studies were carried on NaTaO₃ which serve as a guide to develop visible light active photocatalysts in the future. Novel photocatalysts viz. Bi doped NaTaO₃ and La-Fe co-doped NaTaO₃ were developed which are active to the photocatalytic hydrogen evolution under the visible radiation. The correlation between the synthesis conditions, crystal structure and photocatalytic activities was established by the experimental characterization of the samples as well as detailed electronic structure calculations. In both the photocatalysts, it was found that along with the appropriate band structure, maintaining the ionic charge balance in NaTaO₃ lattice is critically important to achieve visible light photocatalytic activity. This study opens a new venue to develop NaTaO₃ based compounds. It also demonstrates the viability of using computation to design and select visible light active semiconductor photocatalysts.

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Chapter I: Introduction

1.1 Clean energy challenge

The global energy demand is estimated to be doubled by mid of the century [1]. Majority of this demand is driven by the growing population and rising living standards of people across the globe. Conservative speculations suggest that average global power requirements will reach as high as 30 TW by the year 2050, which means that an additional power of 16 TW should be generated in the coming decades [1]. It is a great challenge to meet this energy demand, as the conventional sources of energy i.e. fossil fuels are rapidly depleting. Hubbard Peak Theory predicts that the peak of the oil production will be surpassed in the coming decade and the oil depletion may take place anytime after 2057 [2, 3]. A similar prediction has been stated for the other carbon based fossil fuels. Today, over 95% of the global energy generation depends on the fuels like oil, natural gas, and coal. Thus development of alternative energy technologies, replacing the fossil fuels is inevitable [4]. Sustainable energy solutions that are cost effective, scalable and match the performance of the current energy generation methods are required to meet the future energy needs. Further, over the last century, the use of carbon based fossil fuels has resulted in severe environmental footprints all over the globe. During last decade alone, CO₂ levels has increased by around 15% and the average mean temperature of the surface of the earth has increased by 0.74°C [5]. Research reports predict that continuation of the global warming may cause dramatic effects on the geography, climate and ecosystem of the earth. Thus it is necessary to ensure that power generation and utilization will not contribute to the global warming and has no harmful effect

on the environment in the future. To deal with this serious problem of environmental deterioration and terawatt energy challenge, research in science and technology of clean energy harvesting has gained significant attention worldwide.

1.2 Hydrogen: the fuel of the future

Among the different technologies, hydrogen based energy generation is a promising solution. Hydrogen is considered as one of the potential energy carriers replacing the fossil fuels. Hydrogen has a high gravimetric energy density (140 KJ/g at 350 Bar) compared to the other candidates (Figure 1.1). It undergoes clean combustion resulting in pure water ($2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$; $\Delta G = -123 \text{ kJ/mole}$). The absence of carbon makes its emission CO_2 free, which is advantageous to reduce the greenhouse effect. Hydrogen is abundant in form of water and it is renewable. The primary use of hydrogen as a fuel is intended in fuel cells to produce the electricity. The fuel cells offer clean operation (water as byproduct, absence of NO_x and CO_2) and are known to have high energy conversion efficiency (typically 50 – 60%) [6].

Owing to its unique features, hydrogen based energy generation, storage, and application (hydrogen economy) is considered to be a promising alternative to the fossil fuels. However, hydrogen economy is still in early stages of development and faces many challenges. Among the various challenges, sustainable production of hydrogen is one of the key issues for technology development.

Figure 1.1 Gravimetric energy density of various fuels [4].

The conventional methods of hydrogen production mainly include high temperature steam reforming of methane and other hydrocarbons, chemical reduction of hydrogen containing compounds, thermochemical methods as well as electrolysis of aqueous compounds [7]. These techniques directly or indirectly depend on carbon based fuels as input energy and hydrocarbons as source of hydrogen. Thus these processes are not sustainable and clean for a large scale production of hydrogen. Therefore the production of hydrogen by novels ways that are clean and sustainable is necessary. It is also essential that hydrogen generation is economical and scalable.

1.3 Solar hydrogen

Natural occurrence of pure hydrogen in gaseous form is rare. However, as mentioned earlier, chemically bonded hydrogen is abundantly available in form of numerous compounds existing in the nature. Most importantly hydrogen is abundantly present in form of the water. Utilization of hydrogen trapped in the water molecules is successfully done in photosynthesis reaction by green plants. Photosystem II (PSII) is an enzyme in the plants that splits the water molecules into hydrogen and oxygen using solar energy. While the oxygen is released in the atmosphere, hydrogen is utilized to produce hydrocarbons which can be stored in form of usable energy [8]. Photosynthesis is one of the most successful energy harvesting mechanisms, which indirectly powers the whole living organisms on the planet. Analogous to the photosynthesis, the gaseous evolution of hydrogen and oxygen from the water, over irradiated surface of certain materials is possible and this process is called as photocatalytic water splitting. The splitting of the water molecules into H_2 and O_2 over TiO_2 anode surface under UV radiation was first discovered by Honda and Fujishima [9], often called Honda-Fujishima effect. The phenomenon showed an *alternative approach* to utilize the solar energy to render oxidation and reduction reactions. Since its discovery, this field has been thoroughly studied in depth and breadth. In the recent past, the photocatalysis has shown promising applications in the field of environmental cleaning and clean energy generation. By employing appropriate materials systems as photocatalyst, mass production of hydrogen using solar energy can be economically carried out. The incident solar energy on the earth's surface (3×10^{24} J/year) far exceeds our energy needs [10] and thus allows sustainable energy generation at low cost. The photocatalytic hydrogen generation is simple in operations and mainly uses oxide based catalysts which are cheap and ample in availability. The hydrogen

so produced from water can be used in fuel cells to produce electricity and pure water, making the process recyclable (Figure 1.2). Thus solar hydrogen i.e. hydrogen produced directly from solar energy, is one of the promising approaches for alternative energy generation.

Figure 1.2 Schematics of solar hydrogen: renewable and clean.

1.4 Research scope and objectives

Although there has been intense research in the area of photocatalytic hydrogen production for past four decades, its commercial applications are limited by the poor efficiency of the available materials systems. The splitting of the water into H_2 and O_2 faces many challenges, which demand design of new materials by tailoring their optical and electronic properties. Most of the materials developed till date possess wide band gaps ($E_g > 3.20$ eV) and operate only under ultra violet (UV) radiation. However, the component of the UV radiation in the solar spectrum is very little ($\sim 4\%$), which limits their usage under solar radiation. In order to commercialization the production of the solar hydrogen, a target energy conversion efficiency of 10% is essential [10]. However, a materials system which is stable under oxidizing and irradiated conditions, has a suitable band gap and band edge potentials, and efficient in photocatalytic reactions does not exist. Since the discovery of photocatalytic effect, different materials have been studied, however achieving required efficiencies is still a challenge [10-12]. Therefore, developing new materials with suitable band structure is of immense importance. The band engineering of highly efficient wide band gap photocatalyst is one of the promising strategies to develop visible light active photocatalysts. Earlier research has shown that band engineering of certain catalysts by doping of foreign ions e.g. C, N-doped TiO_2 [13, 14], M-doped $SrTiO_3$ [15], Ni-doped $InTaO_4$ [16], solid solution of ZnO - GaN [17] have achieved significant efficiencies for hydrogen production under visible radiation. Nevertheless, to meet the target efficiencies for commercialization, materials systems with better performance are essential [12].

Among the various wide band gap materials studied, sodium tantalate, NaTaO_3 is known to have high activity for H_2 generation under UV radiation [18-20]. Unlike commonly studied TiO_2 , NaTaO_3 has CB position favorable (sufficiently negative) to the reduction of protons ($\text{H}_2/\text{H}_2\text{O}$). Together with its delocalized nature of photoexcited electrons, this material is beneficial for the photocatalytic hydrogen evolution [21]. Further, NaTaO_3 shows ability to split the pure water into H_2 and O_2 in stoichiometric proportion. Owing to its high activity under UV radiation and characteristic properties, it forms an excellent host material to develop photocatalysts for the water splitting application. It is well known that the optical and electronic properties of the materials can be successfully modified by doping a foreign element in the lattice. Therefore we hypothesize that doped NaTaO_3 photocatalysts hold a good promise for visible light photocatalysis with high energy conversion efficiency. However, in spite of its attractive properties, the studies on visible light driven NaTaO_3 based photocatalysts are limited and the potential of NaTaO_3 as an efficient photocatalyst is not fully explored. In particular, the optical and photocatalytic properties of doped NaTaO_3 are not thoroughly studied. Appropriate modification in the band structure of NaTaO_3 would lead to induce the visible light absorption in this phase while retaining its beneficial photocatalytic properties. Therefore, though pristine NaTaO_3 is not an active photocatalyst under the visible radiation, doped NaTaO_3 would yield higher photocatalytic activities under the visible region. Based on the above literature reading and the hypothesis made, the objectives of this project are summarized as below.

1. Develop NaTaO₃ based photocatalyst capable of absorbing visible light radiation.
 - Identify dopants that would facilitate the visible light absorption in NaTaO₃ through computational studies
 - Synthesize doped NaTaO₃ powders with appropriate dopants
2. Evaluate the materials properties and performance of photocatalyst under the visible radiation
 - Thorough characterization of relevant properties of materials
 - Study the photocatalytic hydrogen evolution and organic pollutant degradation under visible light radiation
3. Understand the role of the crystal structure, microstructure, optical properties, in achieving visible light photocatalytic activity
 - Establish structure-property correlations
 - Understand the mechanism of the band structure alteration

1.5 Organization of the thesis

This thesis is divided into eight chapters. Chapter I provides a background and introduction to the research problem undertaken in this study. Chapter II presents a detailed literature review on the principles of the photocatalytic processes and the photocatalytic materials systems. Chapter III explains the experimental methods of synthesis, characterization, and photocatalytic testing of the doped NaTaO_3 samples. Additionally, the details of the computational methods and models are presented. Chapter IV presents the results of the computational modeling of doped NaTaO_3 systems, carried out to identify the dopants that are useful to narrow the band gap of NaTaO_3 . Chapter V presents the structural and chemical analysis, and optical properties of the bismuth doped powders prepared by solid state route. Further, the photocatalytic performance of the doped powders under visible light irradiation and its correlation with the crystal structure is discussed. Chapter VI presents the photophysical properties of bismuth doped NaTaO_3 nanoparticles prepared by hydrothermal method. Chapter VII presents the results and discussions on crystal structure, optical properties and photocatalytic performance of Fe and La-Fe co-doped NaTaO_3 systems. Finally, the conclusions and the recommendations from this study are presented in Chapter VIII.

Chapter II: Literature Review

This chapter presents the known definitions and mechanisms of the phenomenon of photocatalysis. The important factors affecting the photocatalytic processes are discussed from the point of view of the development of new photocatalyst systems. In particular, effects of doping on the band structure and subsequent photocatalytic activity are discussed in detail. A critical review of the materials systems known so far is presented and materials those have potential to develop efficient catalysts are discussed.

2.1 Definition, overview, and mechanism

Broadly, photocatalysis can be defined as ‘catalysis under irradiated conditions’. It may also include the definition, ‘acceleration of photoreactions’ in presence of light active catalysts [22]. Specifically, on the functional level it comprises oxidation and reduction reactions of various species, initiated by photoexcited electrons and holes over the surface of the irradiated semiconductor [23, 24]. Over the past four decades, photocatalysis has shown promising applications in a wide spectrum of areas. These applications include but not limited to indoor air purification, self cleaning glasses, wastewater treatment, anti-bacterial and antifungal coatings, outdoor photocatalytic paints [23]. Certain catalysts like SrTiO_3 , TiO_2 , have shown promise in reduction of CO_2 to hydrocarbons by photocatalytic process [25-27]. Although the photocatalysis has shown a promise in environmental cleaning applications, one of the main areas of the research is generation of hydrogen via photocatalytic water splitting. The following topics review the fundamentals of

photocatalytic reactions, developments in photocatalysts materials along with the factors affecting the photocatalytic activity.

2.1.1 Mechanism of photocatalytic reactions

A simplified mechanism of photoexcited reactions is shown in figure 2.1. A photocatalyst particle absorbs incident photons which possess higher energy than its band gap and produce photoexcited pairs of electrons and holes. The holes in the VB act as oxidizing agents and reacts with the adsorbed species (S1). Similarly, electrons in the CB reduce the adsorbed species (S2). The photoexcited electrons are in non-equilibrium state and their life time is of the order of a few nanoseconds. Due to the very short lifetime, the electron and hole pairs quickly undergo recombinations reaction. Thus in absence of any acceptor species, the electrons quickly recombine with holes while, in presence of adsorbed species, they are transferred across the semiconductor electrolyte interface.

Figure 2.1 Schematics of the photooxidation and photoreduction reactions [28].

Accordingly to the chemical reactions described above, the photocatalytic water splitting is considered as oxidation of the water molecule and reduction of protons to produce gaseous H_2 and O_2 on the surface of the irradiated semiconductor. The water splitting reaction has a positive free energy of +237 kJ/mol (Figure 2.2).

Figure 2.2 The energy diagram of the formation of water molecule from hydrogen and oxygen [29].

Although the exact molecular mechanism of the water splitting is not known, the speculated mechanism follows a 4-photon model [11, 30]. In most of the cases, to facilitate the water splitting reaction, a co-catalyst is loaded on the surface of the photocatalyst. The co-catalyst helps in separating the photoexcited electron-hole pair as well as suppressing the back reactions in the electrolyte. The photocatalytic water splitting over the photocatalyst, loaded with co-catalyst acts as a short circuited electrochemical cell in which the input energy provided by incident photon as shown in figure 2.3.

Figure 2.3 Schematic of the photocatalytic water splitting over co-catalyst loaded photocatalyst particle.

Chemical reactions for the water splitting are as follows.

(MO is metal oxide photocatalyst, $h\nu$ is incident photon)

The proposed mechanism of the photocatalytic water splitting over co-catalyst loaded semiconductor can be summarized as follows. The water molecule undergoes dissociative chemisorption at the active sites on the surface of the photocatalyst. Upon illumination of

light, a non equilibrium concentration of electrons and holes exist in the conduction band and the valence band of the photocatalyst respectively (Equation 2.1). The electrons near the co-catalyst/photocatalyst (Schottky barrier) interface are directed towards the co-catalyst because of the lower energy states of the co-catalyst. This prevents the recombination of photoexcited electrons and holes. The adsorbed water molecule undergoes oxidation, by donating the electron to the hole in the valence band. Four holes react with two water molecules to form O_2 and $4H^+$ (Equation 2.2). H^+ ions migrate to the co-catalyst surface and react with electron to form H_2 at the active sites on the surface. (Equation 2.3) The above processes/reactions represent a simplified model of the overall water splitting reaction (Equation 2.4). The details of some of the important reactions/processes, their effect on photocatalytic activity and their correlation with the physical properties of photocatalyst are discussed in the following section.

2.1.2 Photoexcitation induced chemical reactions

Figure 2.4 Electrochemical potentials of the red-ox reactions vs. NHE (pH = 7) [24, 31].

The oxidation/reduction potentials of some of the important reactions vs. NHE are shown in figure 2.4. On photoexcitation pairs of electrons and holes are produced in the semiconductor. Considering the semiconductor particle in contact with pure water, oxidation of water to produce hydroxyl ion ($\bullet\text{OH}$) and proton can take place (Equation 2.5). Equations

2.5 to 2.10 show that reactions like formation of hydroxyl radicals and super oxide compete with the direct oxidation of the water and H_2 formation, respectively. These hydroxyl radicals can diffuse in the near surface layers of the electrolyte. They have enough reducing power as compared to the holes. It is proposed that hydroxyl radicals play important role in oxidizing pollutant molecules [6, 7]. Therefore, along with the photogenerated holes, the hydroxyl radicals produced on the photoexcitation are also useful in photocatalytic degradation of pollutants. On account of these photocatalytic reactions, the applications of photocatalysis are mainly focused on photocatalytic hydrogen generation and photocatalytic degradation of pollutants.

2.1.3 Hydrogen production from sacrificial agents

Although the splitting of the pure water splitting is a desired reaction, it has a high kinetic and thermodynamic energy barrier. Therefore, only a few photocatalysts are known to split the pure water into H_2 and O_2 under irradiated conditions. Nevertheless, hydrogen generation is also possible from certain organic compounds like alcohols. Simple alcohols like methanol, ethanol act as sacrificial agents and produce hydrogen according to the equations 2.11-2.14.

Methanol is the most common sacrificial agent which is used to study the photocatalytic hydrogen evolution. It is worth noting that use of methanol is only a kinetic aid and to produce hydrogen from methanol, satisfying the thermodynamic conditions is must. The above reactions indicate that degradation of methanol into hydrogen and carbon dioxide has lower free energy compared to that of the pure water splitting. Kinetically, methanol acts as holes scavenger, thus increasing the rate of reaction. Thus study of hydrogen production from methanol is used to judge the thermodynamic possibility of hydrogen evolution reaction. These sacrificial agents also play an important role in understanding the photocatalytic processes. Methanol itself is a fuel and conversion of methanol to hydrogen is not a sustainable process. However, hydrogen can be generated from other types of waste alcohols, acetones and volatile organic compounds by photocatalysis [32, 33]. Degradation of pollutants and simultaneous generation of hydrogen has gained significant interest as it is way to generate energy from waste [34, 35]. Therefore hydrogen generation in methanol solution is widely studied in the area of photocatalysis.

2.1.4 Photocatalytic degradation of organic pollutants

Photocatalysis has been widely studied to degrade the organic compounds to their simpler forms. In most of the cases, the organic compounds are oxidized by photoexcited holes as well as hydroxyl radicals produced on photooxidation of water. In order to oxidize the organic molecules, the electrochemical potential of holes should be higher than respective oxidation level of the molecule under consideration. Therefore in this case, the potential of the valence band plays an important role. The electrons on the other hand, take part in O_2 oxidation reaction or formation of other complexes. Till date, degradation of several

pollutants like Methyl Orange [36], Methylene Blue[37], Rhodamine B [38], organic acids [39], aromatic compounds (benzene, phenols, chlorophenols) [40, 41], pesticides [42, 43] etc. has been studied. Typically, in order to study performance and efficiency of photocatalysts, Methylene Blue (MB) is taken as a common model pollutant. The photocatalytic degradation is a type of Advanced Oxidation Processes (AOP) and these processes are considered to be useful in waste water treatments. Although every pollutant degradation process may not involve hydrogen evolution, these studies are useful to assess the activity of the photocatalyst for wider applications.

In summary, the photocatalytic reactions are useful in oxidation of the organic molecules in the aqueous media as well reduction of proton to produce the hydrogen. Research work has demonstrated that along with the pure water splitting, hydrogen generation is possible from certain organic compounds. The photophysical properties of the photocatalyst play an important role in determining the feasibility and efficiency of these reactions and thus it is essential to gain the understanding of these properties. The following section reviews critical factors affecting the photocatalytic activity.

2.2 Critical factors affecting the photocatalytic activity

Understanding of the optical and electronic properties of the materials is of immense importance, in order to design and develop efficient catalysts. As mentioned earlier, efficient photocatalysts should be developed by tailoring their properties best suited for a specific application. In this section some of the important properties of the photocatalyst, such as band edge potentials, band gap value, surface area, crystallinity and co-catalyst loading are discussed in relation to their effect on the photocatalytic activity. Further, effect of doping on the band structure and crystal structure is discussed in detail. Although doping has been used to induce visible light activity in wide band gap semiconductors, doping may cause severe distortion in the crystal structure and introduce native point defects which may hamper the photocatalytic activity. Therefore, minimization of these effects should be ensured while designing the photocatalyst.

2.2.1 Band edge potentials

The energy band diagram (NHE scale) of a photocatalyst suitable for the water splitting reaction is shown in figure 2.5.

Figure 2.5 Band diagram of a typical semiconductor and relevant reduction/oxidation energy levels [44].

The band edge potential of a semiconductor is defined as an electrochemical potential of the electrons (or holes) taking part in the photoreduction (or photooxidation) reactions. To facilitate the water splitting reaction, the electrochemical potential of the holes should be more positive than $\text{H}_2\text{O}/\text{O}_2$ oxidation potential of the water and the electrochemical potential of the electrons should be more negative than $\text{H}_2\text{O}/\text{H}_2$ (Figure 2.5). Thus the position of band edge of the semiconductor photocatalyst determines the thermodynamic possibility of the water splitting reaction. The potential differences ΔV_1 and ΔV_2 in the figure 2.5 are termed as overpotentials. Typically, to overcome the kinetic energy barrier, overpotentials of 0.40 eV (each for oxidation and reduction reaction) is required for the efficient photocatalysis [44, 45]. The amount of overpotential also determines the rates of electron and holes transfer across the interface. The schematics in figure 2.6 shows the band potentials (vs. NHE, pH=0) of some of the common photocatalysts [12, 46].

Figure 2.6 The band edge potentials of various photocatalyst vs. NHE [12, 46].

In general, most of the oxide photocatalyst satisfy the condition on the position of the valence band. However, only a few photocatalysts such as ZnS, SrTiO₃, KTaO₃, ZrO₂ have enough CB overpotentials ($E_{CB} > 0.4$ eV) to render the reduction reaction [44]. Enough negative overpotential is beneficial for the photocatalytic hydrogen evolution and thus materials with enough CB potentials are attractive candidates to develop efficient photocatalysts. It is known that the band edge potentials strongly depend on the crystallographic orientation, crystallite and particle size, adsorbed species on the surface (electron/hole trapping), point defects and doping. Therefore the experimental measurements of band edge potentials are essential to understand the factors governing the photocatalytic activity.

2.2.2 Band gap

Taking into account the oxidation potential of the water and the reduction potential of the protons on the absolute energy scale, a band gap of 1.23 eV is essential to facilitate the water splitting reaction. This is the theoretical minimum value required to carry out the reaction. However, as said earlier the kinetic barrier must be taken into consideration and thus a minimum band gap value of 2.00 eV is desirable for the water splitting reaction. Figure 2.7 shows the distribution of the intensity of the solar spectrum with respect to the energy of the photons [47].

Figure 2.7 The intensity distribution of the solar spectrum [47].

It is seen that the practical working range of the band gap should be between 2.00 to 2.80 eV. As mentioned earlier, the band gaps of the most of the oxide photocatalysts such as TiO_2 , SrTiO_3 , ZrO_2 , KTaO_3 ZnS fall in the UV range and thus, under solar radiation these photocatalyst do not exhibit desired performance for the water splitting reaction. Therefore it is essential to develop the materials with the band gap between 2.00 to 2.80 eV to maximize the utilization of the solar energy.

2.2.3 Co-catalyst

Nano sized particles of certain noble metals or certain oxides are deposited on the surface of the photocatalyst to enable photoexcited electron-hole separation. These nanoparticles are typically known as co-catalysts. The co-catalysts are so selected that the Fermi energy of the co-catalyst is positioned below the CB of the photocatalyst and thus the photoexcited electrons are directed from the photocatalyst towards the co-catalyst. In this way, co-catalyst helps separation of electron-hole pairs. Noble metals such as Pt, Au, Pd, Ag are commonly used as co-catalyst to enhance photocatalytic activity photocatalysts like TiO_2 , SrTiO_3 [48-51]. Further, in the water splitting reaction, co-catalyst also serves as H_2 evolution sites which help to separate H^+ ions from O_2 evolution sites preventing the back reaction of the formation of the water. Along with the noble metals, NiO is also known to be effective co-catalysts for the enhancement of the photocatalytic activity for TiO_2 [52], NaTaO_3 [4, 5, 8], InTaO_4 [2], SrTiO_3 [53]. An appropriate selection of the co-catalyst should be done, considering the factors such as type of the contact and band positions. A co-catalyst capable of separating holes from the VB of the photocatalyst serves as O_2 evolution sites. RuO_2 is employed in some cases e.g. ZnO-GaN [54], CaIn_2O_4 , & ZnGeO_4 [54] which is known as

oxygen evolving co-catalyst. It is critical to optimize the amount of co-catalyst loaded on the surface of the photocatalysts. The lower amount of co-catalyst will result in poor separation of electrons and holes while higher amount of co-catalyst may block light absorption by catalyst particle and reduce the photocatalytic activity.

2.2.4 Surface structure, surface area and crystallinity

Photocatalysis is a surface phenomenon and thus larger surface area provides more number of active sites for catalysis, making the process more efficient. In this aspect nanomaterials often offer an advantage in the photocatalysis. Studies on the photocatalytic materials have shown that nano sized materials with large surface area have shown high photocatalytic activity for pollutants degradation as well as hydrogen generation [55, 56]. It is worth noting that along with surface area, crystallinity of the material is also important. Poor crystallinity results in native defects in the crystal which act as electron-hole recombination centers. Such recombinations reduce the number of electrons and holes that would undergo red-ox reactions, thereby decreasing the photocatalytic activity. Apart from these ground state electronic properties, an ideal photocatalyst should possess higher photoconductivity, higher lifetime of photoexcited electrons. Studies have shown that composite structures such as $\text{TiO}_2/\text{C}_3\text{N}_4$ [57], TiO_2/CdS [58], have higher lifetime of electrons.

2.3 Doping for visible light absorption

The photocatalysts that exhibit overall water splitting under UV radiation are good host materials for the modification of the electronic structure to facilitate the absorption of visible light and subsequent photocatalytic activity. Substitutional doping at cation or anion sites has been widely adopted to enhance the visible light absorption. A small quantity of dopant is known to alter the electronic and optical properties of the materials significantly. In the following section, possible mechanisms of visible light absorption and the effect of dopant on the properties of photocatalyst are briefly discussed. In the case of doped photocatalyst, dopant may form additional (other than valence and conduction) electronic states in between the band gap. Depending on the nature of the dopant, these states may be completely or partially filled (near VB, acceptor species) or they may be empty (below the CB, donor species) as shown in figure 2.8. The newly formed electronic states are responsible for reducing the effective band gap (Figure 2.8).

Figure 2.8 Schematics of dopant induced acceptor / donor energy states.

Although doping can be used to facilitate visible light absorption, incorporation of dopant may affect the band edge potentials and native point defect concentration. Therefore it is necessary to assess the effect of dopant incorporation on the electronic and microstructural properties as well as the overall photocatalytic activity of the photocatalyst. The photogenerated charge carriers occupy dopant induced energy states and these states represent effective band potentials of the photocatalyst. If the dopant induced energy states are discrete in nature, the migration of holes or electrons from the points of excitation in the lattice to the surface is difficult which reduces the mobility of charges and it leads to the recombinations of photoexcited electron and holes (figure 2.9). In the case of N doped TiO_2 it is shown that mid-gap states produced are discrete in nature and thus harm the photocatalytic activity [59, 60]. As seen in the schematic (figure 2.9), if the extra electronic states induced by dopants form a band, the mobility of the charge carriers is likely to be higher. The nature of the dopant induced states entirely depends on the interaction of the dopant ions with that of the host ions. Cr doping in SrTiO_3 produces discrete energy states near the VB while the same concentration of Cr in TiO_2 results in the formation of energy band [61].

Figure 2.9 Schematics of energy band vs. discrete electronic states.

In the case of aliovalent doping, introduction of dopant causes ionic charge imbalance in the lattice. To compensate for this charge imbalance, native point defects are produced. These defects may act as recombination centers and contribute to volume recombinations.

In conclusion, the band edge potentials and band gap value are the most important properties of the photocatalysts as they determine the thermodynamics of the specific reaction of interest. It is important to develop materials with the band structure suitable for the water splitting reaction. Doping of the foreign elements is an established technique to induce the visible light activity in wide gap semiconductors; however certain adverse effects of doping should be minimized. The following section reviews the photocatalytic materials systems studied till date. Among the various materials, promising photocatalyst that can be modified to develop efficient photocatalyst is discussed in detail.

2.4 Photocatalyst materials systems

2.4.1 Overview and materials design

Till date, several semiconducting compounds including metal oxides, nitrides and sulfides, have been explored for the photocatalytic hydrogen evolution [10]. A photocatalysts faces strong oxidizing condition as well as photo-irradiation. Under irradiation condition many compounds undergo photocorrosion which results in dissolution of the metal cation in the electrolyte. Thus under these conditions only a few compounds are found to be stable without much degradation in their performance. The oxides photocatalysts are the most stable materials in aqueous environments and under irradiation and thus seen as the most promising candidates to build efficient photocatalysts. Research in early days was focused on TiO_2 and SrTiO_3 based materials. However during last two decades various catalysts for the water splitting as well as pollutant degradation have been studied. In general, certain oxides of Ti, Zr, Ta, and Nb have found to be advantageous for splitting of the pure water. It is noted that simple binary oxides of these d^0 metals may not be active for the water splitting.

Figure 2.10 Schematic of the formation of bands in oxide photocatalyst.

In metal oxides, the conduction band is mainly composed of M (d) or M (p) orbitals while valence band is mainly composed of O 2p orbitals. Therefore, the absolute energy position of the CB is dependent on the d or p orbitals of the constituent metal ion (Figure 2.10). The studies on the materials systems show that, in order to design a photocatalyst suitable for the water splitting reaction, transition metal cations such as Ta, Nb, V, Zr, Ti, Ce, Mo and W (TiO_2 , Ta_2O_5 , ZrO_2) are used to build the crystal structure and energy structure of the photocatalyst. The oxides these elements are found to be able to sustain photocorrosion too. In combination with some alkali ions, alkaline ions or a few d and p block elements complex oxides can be designed to modify the crystal structure. (InTaO_4 , NaTaO_3 , $\text{Cu}_5\text{Ta}_{10}\text{O}_{11}$). However in these compounds the electronic structure remains dominated by former cations. The modification in the electronic structure can be done by doping of anions O, N, S, Se, Cl or certain d or p block cations. Finally co-catalysts can be selected among the noble metals like Pt, Pd, Au, Ag, Ir and Ru for the efficient electron-hole separation. The above mentioned selection criterion serves as general guidelines, that are helpful in designing new catalysts systems. The schematic of the guidelines of the design of the photocatalyst is shown with the help of the periodic table in figure 2.11. Nevertheless, experimental synthesis and testing of the catalysts for photocatalytic performance is essential so as to understand its behaviors and improve its efficiency by optimizing the photophysical properties.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18														
H																	He														
Li	Be											B	C	N	O	F	Ne														
Na	Mg											Al	Si	P	S	Cl	Ar														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr														
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe														
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn														
<table border="1"> <tr> <td>Ce</td><td>Pr</td><td>Nd</td><td>Pm</td><td>Sm</td><td>Eu</td><td>Gd</td><td>Tb</td><td>Dy</td><td>Ho</td><td>Er</td><td>Tm</td><td>Yb</td><td>Lu</td> </tr> </table>																		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																		

Figure 2.11 A guide for the selection of elements for designing efficient photocatalyst for hydrogen evolution [10, 12].

The following sections review the existing literature on the photocatalysts materials in terms of their shortcomings and advantages. Firstly, metal sulfide and metal nitride based photocatalysts are discussed which are followed by detailed review on the oxide photocatalysts. In the oxides photocatalysts the initial part explains the materials systems with narrow band gaps ($E_g < 3.00$ eV), while the later focuses on the wide band gap materials ($E_g > 3.00$ eV) and their modification by doping of the foreign elements.

2.4.2 Sulfide and nitride based photocatalysts

Certain metal sulfides have been studied for the photocatalytic water splitting. CdS (2.40 eV) and ZnS (3.60 eV) based sulfides are extensively studied to improve the visible light activity, and stability [62-64]. Further, catalysts like CuInS₂, AgInS₂, Cu-In-Zn-S₂ [65] loaded with appropriate amount of co-catalyst are known to be active for the photocatalytic hydrogen evolution. Although these classes of materials have demonstrated high yield of hydrogen under visible light, sulfide based catalyst are not capable of splitting the pure water. Further, they are unstable under oxidizing conditions and undergo photocorrosion. To prevent their photocorrosion, additional ions with S²⁻ or SO₃²⁻ as hole scavengers must be provided in the electrolyte. Although sulfides have shown promise for photocatalytic hydrogen generation, their instability and hazardous nature is a major drawback. Similarly, certain nitride compounds such as Ge₃N₄, GaN [66] are active for hydrogen evolution under UV region. Recent studies show that polymeric carbon nitride exhibits photocatalytic hydrogen evolution under visible region [57]. Ge₃N₄ shows overall water splitting with 9% efficiency [66] under UV radiation while Zn-Ge oxynitrides have band gaps in the visible region. Among these compounds, (Zn_{1.44}Ge)(N_{2.08}O_{0.38}) successfully renders the overall water splitting. A solid solution of ZnO-GaN (Rh/Cr loaded) showed overall water splitting with highest energy conversion efficiency of 2.5% [17, 67]. The band gap of GaN-ZnO was reduced by pushing the VB upwards due to Zn 3d- N 2p electrons repulsion. Nevertheless, the nitride based photocatalysts are limited in number and other types of nitrides have shown limited efficiencies. Their stability for longer duration is also not well studied. In short, oxides are best suited and promising candidates for the photocatalytic applications. The present discussion is focused on the oxide based photocatalysts.

2.4.3 Oxides based photocatalysts

Although the semiconductors with the pristine band gaps in the visible region are capable of absorbing solar light, most of these materials suffer from insufficient CB potentials for the hydrogen generation and poor stability under irradiation. Binary oxides like Fe_2O_3 , Bi_2O_3 , Co_2O_3 , and CuO have band gap less than 3.00 eV. However, for all the compounds CB potential is not enough to generate hydrogen and they suffer from photocorrosion. Similarly oxides such as Bi_2WO_6 (2.85 eV), WO_3 (2.80 eV) [12] are capable of evolving O_2 in AgNO_3 solution however fail to produce H_2 . In short, the compounds with pristine band gaps in the visible region do not show promise for the photocatalytic activities under the visible radiation. On the other hand, certain oxides with the band gaps in the UV region ($E_g > 3.00$ eV) have shown excellent stability and photocatalytic activities for pollutant degradation as well as hydrogen generation. Therefore, these wide band gap materials have been studied thoroughly for various photocatalytic applications.

TiO_2 was the first materials to be studied as photocatalyst. Bare TiO_2 (Anatase, P25) do not show overall water splitting in liquid water even under UV radiation, however, the splitting of water vapor was reported [68, 69]. Although TiO_2 demonstrates excellent photocatalytic activity under UV radiation, its performance under visible radiation is restricted due to its band gap value. Therefore cationic and anionic doping in TiO_2 was extensively studied and some of the doped TiO_2 photocatalysts like N, P, C, S. doped TiO_2 , Cr and Sb [70] Fe(III) [71] Ni and Nb,[72] doped TiO_2 showed improved photocatalytic activity for degradation of pollutants under visible radiation. In spite of these efforts, the hydrogen evolution efficiency

of the doped TiO_2 based materials is limited. It is proposed that the point defects in doped TiO_2 produce discrete energy states which modify photophysical properties significantly. The point defects also act as electron-hole recombination centers thus reduce the activity [73]. Similar to TiO_2 certain titanates like SrTiO_3 [25-27] [74], CaTiO_3 (3.5 eV), BaTa_4O_9 , $\text{Sr}_3\text{Ti}_2\text{O}_7$, $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, [75] $\text{La}_2\text{Ti}_2\text{O}_7$: Ba [76], $\text{Y}_2\text{Ti}_2\text{O}_7$ (pyrochlore) [77] were developed which showed high photocatalytic activities under UV radiation.

As compared to the titanates, certain oxides of tantalum have shown higher efficiencies for stoichiometric splitting of the pure water. The valence electronic configuration of Ta is 6s, 5d and thus its valence states lie at lower energies on the absolute scale. Upon hybridization with O2p orbitals, these electronic states would split to form energy bands with the energy positions favorable for the water splitting reaction (enough negative to the reduction potential). Most of the tantalates have band gap ranging from 3.60 eV to 4.50 eV. Ta_2O_5 itself is known to show overall water splitting, when loaded with NiO [78]. Various tantalates have shown overall water splitting without any sacrificial agent, under UV radiation. These compounds include MTaO_3 (M=Li, Na, K) [79], MTaO_4 (M= Cr, Fe, Ln) [33-35], MTa_2O_6 (M=Ni, Mn, Co), $\text{M}_2\text{Ta}_2\text{O}_7$ (M=Sr,Ca) [80]. Along with tantalum oxide based photocatalysts, certain oxynitrides such TaON , LaTiO_2N , CaNbO_2N , CaTaO_2N , LaTaO_2N are developed to evolve H_2 and O_2 evolution in presence of sacrificial agents under visible light [81]. Apart from single phase photocatalyst tantalates have also shown promising applications in so called ‘Z scheme’ photocatalysts. The Z scheme system has two photocatalysts where one of them acts as H_2 releasing phase while the other acts as O_2 releasing phase. To bridge these reactions a redox shuttle is employed. One such systems

consists of Pt loaded N doped SrTiO_3 and RuO_2 loaded TaON which shows promising water splitting activities under visible radiation [82].

In conclusion, the present literature suggests that photocatalysts rendering overall water splitting reaction with significant activities are wide band gap semiconductors ($E_g > 3.2 \text{ eV}$). The photocatalyst with pristine band gap in the visible region have shortcomings of insufficient band edge potentials, chemical stability thus the activity is limited. Compared to the other photocatalysts, tantalates have shown high yield of H_2 and O_2 in pure water (UV radiation). Tantalate based photocatalysts have enough CB potentials for hydrogen evolution. In particular, alkali tantalates have interesting photophysical properties and are highly active for the pure water splitting. The crystal structure and photophysical properties of these material systems are discussed in the next section.

2.5 Sodium tantalate photocatalysts

Alkali tantalates, MTaO_3 ($\text{M}=\text{Li}, \text{Na}, \text{K}$) were first studied by Kato, H. and Kudo, A. in 1998 [83]. These compounds are simple perovskites with large band gap values ($E_g > 3.60 \text{ eV}$). Figure 2.12 shows the crystal structure of MTaO_3 compounds where it is seen that KTaO_3 is a perfect perovskite while NaTaO_3 and LiTaO_3 are distorted octahedra frameworks. It is reported that the degree of distortion increases from KTaO_3 to NaTaO_3 to LiTaO_3 . This distortion results in increase in the band gap values as well as degree of delocalization of photoexcited electrons across the series. High degree of delocalization is beneficial for the mobility of photoexcited charge carriers and thus the photocatalytic activity. Kudo et al.

reported that alkali tantalates are active materials for the photocatalytic water splitting even without loading co-catalysts when irradiated with UV radiation [83]. For the pristine compounds without any co-catalyst, the photocatalytic activity follows a trend as $\text{LiTaO}_3 > \text{NaTaO}_3 > \text{KTaO}_3$. On the other hand upon loading of NiO co-catalyst, NaTaO_3 shows the maximum efficiency for the water splitting reaction.

Figure 2.12 Comparison of the crystal structures and optical band gaps of alkali tantalates [79, 84].

2.5.1 Photophysical properties of NaTaO_3

The measured band gaps and estimated band edge positions of MTaO_3 compounds are shown in figure 2.13. Because of their large band gaps, only UV radiation is required to facilitate the photocatalytic water splitting reaction. As mentioned above, among these

tantalates, NiO loaded NaTaO₃ is known to be more promising candidate than Li and K tantalates. The high activity of NaTaO₃ is attributed to the favorable band conduction band position of NiO and NaTaO₃. It is estimated from the empirical relations that the CB potential lays at around -1.06 eV vs. NHE (pH=0) and that of NiO is at -0.96 eV on the same scale and thus the electron hole separation process is efficient which results in higher activity.

Figure 2.13 Schematic of the band edge potentials of alkali tantalates.

NaTaO₃ is known to exist in two polymorphs viz. orthorhombic (Pbnm, Pcmn) and monoclinic (P₁₂/M₁) under standard temperature and pressure conditions. In its orthorhombic phase it contains Na⁺ cations enclosed in corner shared TaO₆ octahedra (Figure 2.14). In the monoclinic phase, a similar atomic arrangement of seen however, tilting of TaO₆ octahedra is significantly reduced. Both the polymorphs have similar band gap values (~ 4.01 eV) and are known to be active for the pure water splitting reaction. The recent work on orthorhombic phase shows that its photocatalytic activity can be significantly enhanced by doping of certain elements as well as loading of NiO co-catalyst nanoparticles. It is also

observed that the photocatalytic activity depends on the ratio of alkali ion to tantalum in the sample and samples prepared with 5% excess alkali precursor shows a higher activity than those prepared with stoichiometric proportions.

Figure 2.14 Crystal structures of orthorhombic and monoclinic NaTaO₃.

Till date, a few attempts have been made to enhance the photocatalytic activity of NaTaO₃ by doping of suitable ion and loading of suitable co-catalysts. Doping of alkali earth ions (Sr, Ba, Ca) [19] and certain lanthanides (e.g. La, Pr, Nd, Sm, Gd, Tb, Dy) [85, 86] was studied by Kato *et al.* It was seen that addition of lanthanides and certain alkali metals modified the surface morphology of NaTaO₃. Upon doping of these ions, characteristic surface nano-steps appeared as shown in figure 2.15. In a significant development, Kato *et al.* showed that a maximum of 56% quantum efficiency (at 270 nm irradiation) can be obtained from 2% La doped NaTaO₃ loaded with (0.2 wt %) NiO ultra fine particles [21]

Figure 2.15 Surface nanosteps and schematic of NiO loaded La-doped NaTaO₃ [21]

The nanosteps on surface were found to be highly beneficial for the photocatalytic activity. When NiO was loaded on the surface, NiO particles selectively occupied the sharp corners on the steps, thus separating the sites for H₂ and O₂ evolution. This unique microstructure was helpful in preventing electron hole recombination as well as undesirable back reaction in the electrolyte. Therefore it is highly desirable to produce this unique microstructure in a photocatalyst which is active to the visible light.

2.5.2 Visible light driven NaTaO₃

Till date, studies on the visible light active sodium tantalates are limited. Nitrogen doped NaTaO₃ catalyst has been studied for the visible light driven photocatalytic degradation of Methylene Blue as well as gaseous formaldehyde [87]. Co-doping of cations such as Cr-La [88] doped NaTaO₃, Ir-La doped NaTaO₃ [89] have been studied for visible light driven hydrogen evolution. A solid solution photocatalyst (Na_{1-x}La_xTa_{1-x}Co_xO₃ for x=0.0 to x=0.25) have been developed to tune the band gap to the visible region that showed hydrogen

evolution from aqueous methanol solution [90]. These studies suggest that visible light absorption can be achieved by the modification of the band structure via substitutional doping of appropriate cations at Ta site in NaTaO₃ lattice. Recently, Bismuth doped NaTaO₃ nanoparticles prepared by hydrothermal method have been studied for photocatalytic reactions. Li et al. reported a visible light active solid solution photocatalyst i.e. NaTa_{1-x}Bi_xO₃. [91]. The driven hydrogen evolution over these nanoparticles took place without any co-catalyst loading. The optical absorption properties of Bi³⁺ doped NaTaO₃ nanoparticles were also studied by Wang et al. where a small change in the band gap of NaTaO₃ was seen upon Bi doping. Doping of foreign elements is one of the most successful ways to alter the band structure of the host material and induce visible light absorption. Therefore, detailed studies on impurity doped NaTaO₃ and their photocatalytic activities are important in order to develop NaTaO₃ based photocatalysts for solar energy application.

2.6 Summary

In conclusion, visible light active NaTaO₃ based photocatalysts are limited to few systems and their photocatalytic activities are low. While NaTaO₃ system holds a good potential to develop efficient water splitting photocatalyst, study of doped NaTaO₃ system is lacking in the literature. A design of photocatalysts with appropriate band structure (absorption of visible light and enough overpotential) is essential for the water splitting reaction and such design is possible on account of high overpotentials of sodium tatalate. Owing to the favorable band potentials and other beneficial factors (non-thermodynamic), NaTaO₃ based photocatalysts are promising candidate materials to perform band engineering. Therefore in

this study development of photocatalysts with NaTaO_3 as a host material is carried out. Using various experimental techniques and DFT based band structure calculations doped NaTaO_3 photocatalysts which are active to visible light are studied.

Chapter III: Methods

This chapter describes the computational models and methods used to study the band structures of doped NaTaO_3 systems. The experimental methods of synthesis, characterization and testing of the doped NaTaO_3 powders are also explained. Along with photocatalysts synthesis, methods of loading of co-catalysts are described in detail.

3.1 Band structure calculations

3.1.1 Computational methods

In an effect to select appropriate dopant(s) and to understand the band structure of doped and co-doped NaTaO_3 , Density Functional Theory (DFT) based *Ab-initio* calculations were carried out on the models, which were close to the experimentally synthesized NaTaO_3 materials [92]. All the calculations were performed using Cambridge Series Total Energy Package (CASTEP) [93] as implemented in Materials Studio 5.0. The exchange-correlation functional was constructed by the Generalized Gradient Approximations (GGA) proposed by Perdew and Wang (PW91) [94]. Ionic interactions in the lattice were modeled by ultrasoft pseudopotentials method. An energy cutoff of 400 eV was employed to describe the electronic wavefunctions with a plane-wave basis set. The Brillion zone was sampled by Γ point centered Monkhorst–Pack k -points mesh of $2 \times 3 \times 2$ for geometry optimization and $3 \times 4 \times 3$ for the calculation of Density of States (DOS). The values of the energy cut off (400

eV) and K points ($2 \times 3 \times 2$) were tested for the total energy convergence criterion. A complete geometry optimization i.e. atomic positions and lattice parameters (a, b, and c) was carried out on the pristine and doped NaTaO_3 structures. It was ensured that the forces on individual ions in the optimized structure were below $0.05 \text{ eV/\AA}$ and total stress was less than 0.05 GPa. The lattice parameters were optimized in an anisotropic manner.

3.1.2 Computational models

Figure 3.1 A supercell of orthorhombic NaTaO_3 consisting 80 atoms.

The experimentally reported crystal structure of orthorhombic NaTaO_3 (Space Group No. 62 Pcmn) was used as the initial structure [92]. A super cell of $2 \times 1 \times 2$, consisting of 80 atoms was constructed and substitutional doping or co-doping of foreign elements was studied using this supercell (Figure 3.1). A substitution of a dopant ion at one of the cation sites accounts for 6.25% doping, while a pair of co-dopants at two cations sites, accounts for doping of

12.5% by moles. The calculated lattice parameters of the pristine NaTaO₃ structure (5.6238 Å, 7.8915 Å and 5.5223 Å), are in good agreement with the experimental data [95]. In order to understand the changes in the band structure, total density of states and site projected partial density of states (s, p, d orbitals) of the pristine and doped structures were plotted.

3.1.3 Band gap issue

It is known that the DFT calculations systematically underestimate the band gap values of the semiconductors by around 30 to 40%. This underestimation is attributed to the shortcoming of exchange-correction functionals used to describe excited states. Density functional theory is strictly applicable to the ground state electronic systems. In semiconductors, the conduction band edge energy states are considered as excited states, as the electron occupy only up to the valence band under non excited conditions. Therefore, a systematic error is introduced in the calculations of CB energies. However, this error can be corrected to match the experimentally observed band gap values by a few known methods such as linear scaling (scissor operator), GW approximation [96], onsite coulomb potentials (GGA+U or LDA+U) [97]. The use of GW approximations and onsite columbic potentials are computationally expensive and thus in the present calculations scissor operators are used to correct the band gap values. It is worth noting that the relative results of the calculations carried out using the same set of parameters are known to be reliable. Thus the pristine and doped structures can be meaningfully compared in terms of change in the band gap energies. Earlier studies have shown that relative comparison in the band gap energies can be studied irrespective of the known limitation of DFT [98, 99]. In the present calculations, a scissor operator of 1.88 eV was applied to all the band structures and DOS calculations.

3.2 Solid state synthesis

Pristine and doped NaTaO_3 powders were prepared by mixings Ta_2O_5 (Alfa Aesar, Aldrich >99%), Na_2CO_3 (Univar 99.8%) and oxide of the selected dopant (Bi_2O_3 for Bismuth doping, Aldrich >99%, Fe_2O_3 for Iron doping Alfa Aesar, and La_2O_3 for La-Fe co-doping, Alfa Aesar) in varying stoichiometric proportions. The starting materials were mixed in agate type mortar, ground thoroughly using acetone, pressed into pellets and heated at 1173 K for 10 hours using a platinum crucible placed in a muffle furnace in ambient atmosphere. A series of samples with dopant content of up to 10% (by moles) was synthesized as mentioned above. In the case of Bismuth doping, the samples were prepared under three different condition viz. strongly Na-rich ($\text{Na/Ta} > 1$), mildly Na-rich ($\text{Na/Ta} \sim 1$) and Na-deficient ($\text{Na/Ta} < 1$). These conditions were employed by adjusting Na/Ta ratio in the starting materials. In the case of pristine NaTaO_3 , Fe and La-Fe co-doping, the samples were prepared with 5% excess Na_2CO_3 , as the compounds of Na have tendency to evaporate at high temperatures. In all the cases, the final powders were washed with deionized water and dried below 100°C.

3.3 Hydrothermal synthesis

Pristine and Bi doped NaTaO₃ samples were also prepared by hydrothermal method. Starting materials Ta₂O₅ (Alfa Aesar, > 99%), NaBiO₃ (Aldrich 99%), and NaOH (Aldrich 99%) were mixed together in a beaker and stirred for 2 hours. This solution was then transferred to a Teflon autoclave with steel casing. The hydrothermal treatment was carried out for 24 hours in an oven at 200 to 250°C. The samples were thoroughly washed with deionized water to remove excess alkali and dried below 100°C. The samples with different Bi concentrations of 2.5, 5.0, 7.5, and 10% (by moles) were synthesized as mentioned above. In addition, the samples were also prepared with different NaOH concentration in the same manner as explained above.

3.4 Co-catalyst loading

Nanoparticles of platinum were loaded on the surface of the catalyst by chemical impregnation method as well as photodeposition method. In chemical impregnation method an appropriate amount of catalyst powder and platinum precursor (H₂PtCl₆ · 6H₂O, Sigma Aldrich, ACS grade) were mixed in an agate type mortar. The suspension was continuously stirred and heated at 75°C till it dries. The powder was further heat treated at 250°C for 1 hour in alumina crucible to allow the co-catalyst to crystallize and grow on the surface of the catalyst powder. In the case of photodeposition method, the catalyst powder and appropriate amount of platinum precursor (H₂PtCl₆ · 6H₂O, Sigma Aldrich, ACS grade) were mixed with 50% methanol solution in a beaker. This suspension was irradiated for 6 to 8 hours by UV

lamp (Asahi 320) under constant stirring. The solution was washed and filtered out to collect the powders which were subsequently dried at 120 °C for two hours. The chemical impregnation method was used for Bi doped NaTaO₃ powders while the photodeposition method was used for Fe and La-Fe co-doped NaTaO₃ powders.

3.5 Crystal structure and phase development

The crystal structure of the samples was studied by X-ray Diffraction technique (XRD). XRD patterns were recorded using Bruker D8 Advance (Cu K α =1.54 Å) within 2 θ range of 10° to 120° with the steps of 0.01° at a scan rate of 1 second per step. The Rietveld refinement of XRD patterns was carried out using Topaz 3.0. In the refinements, profile parameters such as background function (a five term Chebychev polynomial), zero corrections, scale, and structural parameters such as lattice constants, crystallite size, strain, isothermal parameters, and site occupancies were refined in appropriate order. Appropriate models of crystal structure were selected for the refinements. The location of dopants in the lattice was determined from the site occupancy values obtained from the refinements results. The compositions of phases in the samples were determined from the weight fraction method as indicated by the Rietveld refinement.

3.6 Chemical analysis

To determine the formal oxidation states and chemical environment of the constituent elements in the sample, X-ray Photoelectron Spectroscopy (XPS) (Kratos Axis –ultra, Al_{Kα} source) was carried out. The analysis of the XPS spectra was carried out by fitting the peaks to the Gaussian functions facilitated in software CASA. C 1s reference of 284.5 eV was chosen for calibration. The concentration of elements in the final products was estimated by Energy Dispersive Spectroscopy (EDS) analysis carried out using JOEL 6360 scanning electron microscope. ZAF method for standard-less quantitative analysis was used for elemental analysis. The ratio of Tantalum to dopant ion was recorded to estimate the concentration in molar percentages.

3.7 Microstructure, surface area, and optical properties

Morphologies of the pristine and doped photocatalysts were studied by scanning electron microscopy (JOEL 6360). The changes in particles shape and surface profiles were studied by high magnification secondary electron images, recorded using field emission scanning electron microscope (FESEM, JOEL 6400F). The high resolution transmission electron micrographs (HRTEM) and bright field images were recorded using transmission electron microscope (JOEL 2100F). The optical absorption properties of the powders were studied by Diffused Reflectance Spectroscopy (DRS) (Perkin Elmer 900 UV-VIS Spectrometer). The band gap values were estimated by Kubelka-Munk plots assuming direct band gaps for NaTaO₃. The surface area of the samples was estimated by Brunauer, Emmett, Teller (B.E.T)

techniques. Adsorption isotherms were recorded at -196°C after 6 hours of degassing, to investigate the surface area as well as porosity in the samples.

3.8 Photocatalytic tests

The photocatalytic hydrogen evolution tests were carried out in a closed-gas circulation system (schematics shown in figure 3.2). The reaction cell was made up of Pyrex glass with a quartz window suitable for vertical illumination. A 1000 W high pressure Xe lamp (Oriole Instruments, USA) was used as a light source. A 390 nm cut off filter was employed to screen the deep UV light for the hydrogen evolution reaction. The average intensity at the surface of the solution was measured to be 150 mW/cm^2 . The IR component in the radiation was removed by circulating water filter. The reaction temperature was maintained at 25°C by the help of external water circulation jacket. The air in the reaction cell was removed by purging the argon gas before experiment. In all tests, 50 mg of catalyst was suspended in 80 mL deionized water and 20 mL methanol by magnetic stirring. The reaction was carried out for 12 hours and the amount of hydrogen evolved was analyzed at every two hours by gas chromatograph (Shimadzu GC-2014; Molecular sieve 5A, TCD detector, Ar carrier gas). It was confirmed that no hydrogen was evolved under dark conditions and without addition of catalyst.

The photocatalytic behavior of the pristine and Bi doped powders was also studied by photodegradation of Methylene Blue (MB) in a batch type reactor. In all experiments, 25 mg of catalysts was suspended in 50 mL of 20 ppm MB solution by magnetic stirring and was

vertically irradiated using a 300W lamp (Asahi 320) with internal IR reflector filter. The radiation was restricted to the visible region by a 420 nm cut-off filter. The solution was sampled every hour and centrifuged to filter out the catalyst particles before UV-Vis measurement (Shimadzu 2100 spectrometer) to determine the concentration of MB. The blank test was carried out on 20 ppm MB solution without adding any catalyst. In addition, change in the MB concentration under dark conditions was tested for all catalysts as a reference.

Figure 3.2 Schematics of the photocatalytic water splitting reactor.

Chapter IV: Dopant Selection by Computation

This chapter presents the results of the computational modeling carried out within the framework of Density Functional theory (DFT). Pristine and doped NaTaO₃ structures are optimized for the ground state geometry and their density of states are plotted subsequently. The alterations in the band gaps of each system are systematically analyzed by studying the density of states plots. Based on these results, dopants which are useful for narrowing the band gap of NaTaO₃ are indentified and considered for the experimental synthesis.

4.1 Computational studies on photocatalysts

Modeling of materials based on quantum chemical methods, is a powerful tool to understand and predict some of the fundamental properties of materials such as thermodynamic properties, ground state electronic structure, vibrational properties, mechanical properties etc. Recent advances in the materials systems have generated significant interest in the electronic structure calculations of a wide range of materials. Among the different methods used to study the electronic structure, Density Functional Theory (DFT) based calculations are one of the most popular and versatile methods. DFT based electronic structure calculations are extensively applied to gain the understanding of the optical properties of various materials systems. In the field of photocatalysis, electronic structure calculations are carried out for various purposes which include but not limited to, study the effects of dopants on band structure, study the band structure of new phase, study the thermodynamics

of native point defects, investigate the effect of point defects on the band gap etc. In particular, DFT calculations have proved to be useful to understand the valence electronic structure (band structure) of doped photocatalysts which plays a critical role in the visible light photocatalytic activity. Earlier studies have shown that the origin of the visible light activity can be successfully explained by DFT calculations for several doped photocatalyst such as N, S, P, C, Fe, B and Cu doped TiO_2 [99-105], N and Cr doped SrTiO_3 [106, 107], Cu doped CaTiO_3 [108], Ni doped InTaO_4 [109]. However the DFT modeling is not only limited to the understanding and explanation of the existing systems but can be used to *predict* the optical properties of new materials systems. The band structure calculations performed on appropriate models can be used to predict the changes in the band gap values when foreign elements are doped in a particular phase of interest. Therefore in this study, we have carried out extensive band structure calculations on doped NaTaO_3 systems. The calculations are carried out on a set of selected dopants. The goal of the present study is to identify suitable dopants in NaTaO_3 which are potential candidates for the visible light absorption and subsequent photocatalytic activity. This effort thus guides the experimental work on doped NaTaO_3 systems.

4.2 Computational studies on NaTaO_3

The electronic structure of the pristine NaTaO_3 (orthorhombic and monoclinic) has been well studied by DFT calculations. The band gap of the orthorhombic NaTaO_3 is reported within the range of 2.3 to 2.6 eV by calculations using GGA functionals [110, 111]. Among the doped NaTaO_3 systems, the computational studies on the anionic (N, F, P, Cl, and S)

doping are reported by Han et al. [112]. This study shows that certain anion such as P could be useful for the visible light absorption [112]. Cobalt doping in NaTaO₃ produces Co 3d derived electronic states that are responsible for a band gap narrowing of around 1.00 eV [90]. DFT calculations of N doping in NaTaO₃ suggest, N 2p states appear above the valence band and thus effective band gap is reduced by 0.4 eV [87]. Although N and Co doping has been experimentally reported, photocatalytic activities of these compounds are low. The present literature suggests that investigations on the optical properties of doped NaTaO₃ are limited to only a few dopants. In order to explore the potential of NaTaO₃ photocatalyst and build an efficient materials system, effect of a range of dopants should be studied in detail. Both computational and experimental investigations on the effect of dopant on the band structure and photocatalytic activity are essential.

4.3 Computation based design

Taking into account three intrinsic properties of dopant ions, viz. ionic radii, electronegativity, and oxidation state (ionic charge balance), a set of dopants was selected for the calculations. It is known that the valence band structure of NaTaO₃ is mainly determined by Ta and O ions. Thus replacement of Ta or O ions by dopant ions is likely to affect the valence band structure significantly. Tantalum ions are present in Ta⁵⁺ (0.64 Å) oxidation state, in six-fold oxygen coordination. Considering the above mentioned factors, certain transition metal ions such as Titanium (Ti), Chromium (Cr), Manganese (Mn), Iron (Fe), Yttrium (Y), Tungsten (W), Copper (Cu), and Nickel (Ni), certain p block elements Bismuth (Bi), Antimony (Sb), Indium (In), and Tin (Sn), and certain anions viz. Nitrogen

(N) and Sulfur (S) are selected as dopants. Additionally, effect of a rare earth element Cerium (Ce) is also studied. The band gap of pristine NaTaO₃ obtained by the optical measurements is around 4.01 eV. Thus to enable visible light absorption, a band gap reduction of around 1.00 eV is essential.

4.4 Density of states and band structure of pristine NaTaO₃

Pristine NaTaO₃ is a direct band gap semiconductor as shown in figure 4.1, where the minima and maxima of the bands occur at G point in the First Brillion Zone. Figure 4.2 shows the partial Density of States (DOS) of the pristine NaTaO₃. The analysis of DOS plots shows that top of the valence band (VB) is predominantly composed of O 2p while the conduction band (CB) mainly consists of Ta 5d orbitals. Thus upon the photoexcitation the transition of electrons from O 2p to empty Ta 5d orbitals occurs. The band gap value of this structure is found to be 2.13 eV, which is in agreement with the reported literature [113].

Figure 4.1 Band structure of orthorhombic NaTaO₃ showing a direct band gap.

The calculated band gap value is much smaller than the experimental value due to the well-known under-estimation of the band gap by standard DFT. In order to match the computationally calculated band gap value to that obtained from the experimental measurements (4.01 eV), a scissor operator of 1.88 eV is applied to the band structure and the DOS plots. This operator is also applied to other doped systems to compare the band gap values meaningfully and estimate the quantitative changes in it.

Figure 4.2 Partial density of states (PDOS) of pristine NaTaO₃ showing the composition of the valence and conduction band

4.5 DOS analysis of doped NaTaO₃ systems

Figure 4.3 shows the DOS plots of NaTaO₃ doped with 3d transition metals (Ti, Y, Fe, Mn, and Cr). It is observed that the extra energy states are induced in between the band gap for Fe, Mn and Cr doping.

Figure 4.3 Partial density of states of transition metal (Ti, Y, Fe, Mn, and Cr) doped NaTaO₃ (the dashed line represents the Fermi energy).

These energy states are mainly composed of M 3d and O 2p orbitals and they are responsible for an effective band gap reduction of 0.93, 1.10 and 1.60 eV for Fe, Mn and Cr doping respectively. The experimental work on Cr doping indeed shows the appearance of extra peaks in diffused reflectance spectra leading to the extension of visible light absorption up to 650 nm [88]. On the other hand, Ti and Y doping do not alter the band structure significantly. Ti 3d and Y 3d energy states mix with O 2p energy states and additional states are created above the VB. However, the effective decrement in band gap value is limited only to 0.10 eV and 0.12 eV for Ti and Y, respectively. Figure 4.4 shows the partial DOS plots of NaTaO₃ structures doped with metals Ce, W, Ni, and Cu.

Figure 4.4 Partial density of states of metal (Ce, W, Ni, and Cu) doped NaTaO₃ (the dashed line represents the Fermi energy).

It is observed that doping of Ce and W alters the band structure of NaTaO₃ by inducing additional energy states below the CB. The site projected DOS analysis shows that Ce 4f and W 5d derived energy states reduce the effective band gap value by 0.25 eV and 0.06 eV respectively. In the case of W doping, the Fermi energy of the system was found to be present at the bottom of the CB. The change in Fermi energy position occurred due to presence of excess electron when W⁶⁺ is doped at Ta⁵⁺ site. Doping Cu and Ni produces energy states above the VB in between the band gap and the effective band gap value is found to be diminished by 0.80 eV and 1.20 eV respectively. The partial DOS plots of NaTaO₃ system doped with p block elements are shown in figure 4.5.

Figure 4.5 Partial density of states of p block elements (In, Sb, Sn, and Bi) doped NaTaO₃ (the dashed line represents the Fermi energy).

The DOS analysis shows that Sn doping decreases the band gap value by 0.05 eV while In doping reduces the band gap by 0.10 eV. The substitution of Sb at Ta site leads to increase in the band gap value by 0.15 eV. It is clear that doping of Sn, In, and Sb has insignificant effect on the alteration of the band gap. On the other hand Bi doping creates Bi 6s induced energy states below the CB, resulting in narrowing of the band gap by 0.76 eV.

Figure 4.6 Partial density of states of anion (N and S) doped NaTaO₃ (the dashed line represents the Fermi energy).

Figure 4.6 shows the DOS plots of N and S doped NaTaO₃. It is observed that for nitrogen doping, N 2p induced electronic states appear above the VB, however their contribution in reducing the effective gap is limited only up to 0.45 eV. The effect of S doping on the band gap is found to be more significant than nitrogen and the gap is effectively reduced by 0.75 eV. A summary of the effective band gap values of the doped NaTaO₃ systems is presented

in Table 4.1. We will use these calculation results as a guideline to select dopants for the experimental work.

Table 4.1 The effective band gap values of doped NaTaO₃

Dopant	Effective Eg (eV)	Dopant	Effective Eg (eV)
Cr	2.41	Ce	3.95
Mn	2.91	Y	3.89
Fe	3.08	Bi	3.25
Cu	3.21	N	3.56
Ni	2.81	S	3.26
W	3.76	In	3.91
Ti	3.91	Sb	4.16
Sn	3.96	Ga	3.71

4.6 Dopant selection

Table 4.1 shows that elements such as Sb, In, Sn, Ga, Ce, and Ti do not change the band gap value significantly. Therefore these metals are not considered to be useful dopants for NaTaO₃. Although W and Ce could narrow the band gap values to certain extend, this narrowing is not sufficient for the visible light absorption. Thus W and Ce are out of consideration as well. 3d transition metals, such as Mn, Cr, Fe, Cu, and Ni, could effectively narrow the band gap of NaTaO₃ and thus shift the absorption to visible region. Among these

metals, doping of Co and Cr into NaTaO₃ has been studied earlier. Indeed, these doped NaTaO₃ powders show visible light absorption. However, the photocatalytic activity of these compounds was found to be low under visible light radiation [88, 114]. Both Cr and Mn are multivalent ions and they may act as electron-hole recombination centers and hamper the photocatalytic activity. Therefore Mn doping is not considered in the present study. Further, substitutional doping of Cu or Ni at Ta site would lead to the formation native point defects such as vacancy of oxygen or cation interstitials and cause severe lattice distortion. Thus Cu and Ni doping is not taken into account for the experimental work. Among the transition metals, Fe is selected for further experimental investigations based on two considerations. First, Fe doping can narrow the band gap of NaTaO₃ and second, LaFeO₃ is very likely to form solid solution with NaTaO₃. It is known that La-doped NaTaO₃ exhibit high photocatalytic activity under UV irradiation [86]. Thus we hypothesize that co-doping of La and Fe in NaTaO₃ could be beneficial for the visible light photocatalytic activity. Among p block elements, Bi doping can significantly narrow the band gap of NaTaO₃. Although bismuth induced states appear below the CB, the CB potential of NaTaO₃ is sufficiently negative to the reduction potential of protons. Furthermore, bismuth ions can exist in Bi³⁺ as well as Bi⁵⁺ form thus it can occupy either Na⁺ or Ta⁵⁺ sites. Although anion like S may be useful for the visible light absorption, anionic doping of S may not be stable under oxidizing conditions and long term stability of S doping may be an issue, thus anionic doping is not pursued in this work. To the best of our knowledge detailed investigations on La-Fe co-doped NaTaO₃ and Bi doped NaTaO₃ systems are not reported in the literature and these studies will contribute to the understanding and development of NaTaO₃ based photocatalysts.

4.7 Roadmap of experimental investigations

Among the various elements studied by DFT calculations, Bi and Fe will be selected as dopants in NaTaO₃ for the experimental investigations. Bi³⁺ (1.03 Å) and Na¹⁺ (1.02 Å) have similar ionic radii for XII oxygen coordination [115] and on the other hand, Bi (2.02) and Ta (1.5) have similar electronegativity values. Therefore, it is speculated that bismuth ions could occupy Na or Ta sites in the lattice, giving rise to different stoichiometries of Bi doped NaTaO₃ powders. In order to explore the possibility of occupancy of Bi ions at both Na and Ta sites, the samples with controlled stoichiometry (different Na/Ta ratio) are planned. Bi doped NaTaO₃ powders will also be prepared by low temperature hydrothermal route. There are two considerations for using the low temperature route. First, the low temperature route offers an advantage of high surface area (nano sized particles) and second, the use of NaBiO₃ (Bi⁵⁺) as the precursor of bismuth provides a possibility of substitution of Bi⁵⁺ (0.76 Å) at Ta⁵⁺ (0.64 Å) in the lattice.

Similarly, Fe doped and La-Fe co-doped NaTaO₃ powders will be prepared by the conventional solid state route. Co-doping of La (at Na site) and Fe (at Ta site) will be carried out so as to maintain the ionic charge balance in the lattice and thus help improve the photocatalytic activity as compared to Fe doping alone. Chapter V to Chapter VII presents the results and discussion on the experimental investigations on the doped NaTaO₃ samples.

Chapter V: Bi doped NaTaO₃ - Solid State Route

5.1 Introduction

This chapter presents the results and discussion on the crystal structure, chemical analysis and optical properties of bismuth doped NaTaO₃ samples prepared by the solid state route. The photocatalytic performance of the samples under the visible light radiation is studied for Methylene Blue (MB) degradation as well as hydrogen evolution. Apart from the calculations carried out in the earlier chapter, additional DFT calculations are performed on Bi doped NaTaO₃ structures with Bi at Na, Ta and both Na and Ta sites, in order to explain the observed optical properties of the experimentally synthesized samples. The correlation between the synthesis conditions, the location of bismuth in the lattice, and the optical properties is discussed.

The band structure calculations showed that doping of bismuth at Ta site in NaTaO₃ causes extra states in the band gap and these states could be responsible for the visible light absorption. Bismuth doping in wide band gap semiconductors has been studied for certain materials like TiO₂ and ZnO in order to tune their optical properties [116]. Further, it is known that oxides of bismuth have narrow band gaps on account of Bi 6s orbitals [117, 118]. Therefore, based on the DFT calculations and literature reports, bismuth doping in NaTaO₃ is expected to extend the absorption spectra in the visible region.

5.2 Crystal structure

In the solid state synthesis of Bi doped NaTaO₃ powders, the stoichiometry of the initial reactants i.e. Ta₂O₅, Bi₂O₃ and Na₂CO₃ was varied by changing the molar ratio of Ta₂O₅ and Na₂CO₃. The synthesis conditions of Bi doped NaTaO₃ powders are summarized in Table 5.1. The samples prepared in the above stoichiometric ratios were characterized to understand their structural and photo-physical properties. The samples prepared under strongly Na-rich conditions (Na/Ta > 1) are assigned to series S1, Na-deficient conditions (Na/Ta < 1) are assigned to series S2 and those prepared under mildly Na-rich conditions (Na/Ta ~ 1) are assigned to series S3.

Table 5.1 Ratios of the initial reactants used to synthesize Bi doped NaTaO₃ samples

	Ta	Na	Bi
Series 1 (S1)	1-x	1	x
Series 2 (S2)	1	1-x	x
Series 3 (S3)	1	1.01-1.03	x

(x is the fraction of bismuth content)

X-Ray Diffraction (XRD) patterns of the pristine NaTaO₃ conformed to space group No. 62 Pbnm (JPCDS card No. 01-089-8061). The refined lattice parameters and unit cell volume (a=5.4834 Å, b=5.5228 Å, c= 7.7933 Å; V= 236.012 Å³) of the pristine NaTaO₃ were in good agreement with the values reported in the literature [92]. The XRD patterns of Bi

doped samples in all the series S1, S2 and S3 also belonged to the space group No. 62 (Pbnm). The samples in the series S1, S2, and S3 showed presence of monophasic up to 7.5% bismuth doping when trace amounts of impurities started to appear (Figure 5.1 to 5.3). The impurities became prominent for 10% Bi doping, indicating that for all the synthesis conditions, 7.5% was the solubility limit of Bi ions in NaTaO₃ lattice. For 10% Bi doping, impurity phase of Bi₂O₃ was present for series S1 (Figure 5.1) while appearance of reduced bismuth oxide (Bi₂O_{2.33}) phase was evident in series S2 (Figure 5.2). The samples in series S3 however, showed the presence of Bi₂O₃ in small proportion compared to that of S1 and S2 (Figure 5.3).

Figure 5.1 XRD patterns of Bi doped NaTaO₃ in the series S1 with Bi content (a) 0%, (b) 2.5%, (c) 5%, (d) 7.5%, and (e) 10%.

Figure 5.2 XRD patterns of Bi doped NaTaO₃ in the series S2 with Bi content (a) 0%, (b) 2.5%, (c) 5%, (d) 7.5%, and (e) 10%.

Figure 5.3 XRD patterns of Bi doped NaTaO₃ in the series S3 with Bi content (a) 0%, (b) 2.5%, (c) 5%, (d) 7.5%, and (e) 10%.

Figure 5.4 shows the variation in the unit cell volumes of the doped samples obtained from the Rietveld refinements of the XRD patterns. The samples in all the series showed increment in the cell volumes along with the increase in bismuth concentration. Further, it was observed that the changes in the unit cell volumes were sensitive to the synthesis conditions. A maximum increase in the unit cell volumes was seen for the samples prepared under Na-deficient conditions (S2), followed by those prepared under strongly Na-rich (S1) and mildly Na-rich conditions (S3), respectively. The changes in the unit cell volume are compounded effects of the dopant accommodation and presence of native point defects in the lattice. Therefore, it is clear that changes in the synthesis conditions were responsible for the observed cell volume changes. It was further seen that the Vegard's law was not followed for any of the lattice parameters, indicating that doping may not have been uniform in the lattice.

Figure 5.4 Variations in the unit cell volumes along with increase in Bi content in series S1, S2, and S3.

Figure 5.5 Variations in the unit cell volumes along with the changes in Na/Ta ratio for 5% Bi doping.

To gain the understanding of the changes in the cell volumes with change in Na/Ta ratio, a comparison of the cell volumes of the samples in series S1, S2, and S3 for fixed (5%) bismuth content was carried out (Figures 5.5). Additional samples with Na/Ta ratio of 0.98 and 1.02 were synthesized and analyzed for the same. In the case of the fixed Bi content and varying Na/Ta ratio, under the Na-deficient conditions (S2), significant increment in the unit cell volume was observed. As the conditions became Na-rich, the cell volume expansion was seized while after a certain Na/Ta ratio the cell was again expanded. These results indicated that synthesis conditions markedly affect the stoichiometry of the compounds. Along with the native point defects, synthesis conditions could also change the occupancy of Bi ions at Na and Ta sites.

5.3 Crystal defects

In the crystal structure of the doped samples, Bi ions are likely to occupy only Na or Ta sites in the lattice. NaTaO₃ (Pbnm) is a close packed structure thus the possibility of interstitial is eliminated. The possible charge neutrality equations of Bi accommodation at Na and Ta sites in NaTaO₃ lattice are summarized as follows.

$$(\text{Na}^+) = (\text{Bi}^{3+}) - 2 (\text{Na}^+) \quad (5.1)$$

$$(\text{Na}^+) = (\text{Bi}^{3+}) - (\text{Ta}^{5+}) + (\text{Na}^+) - (\text{O}^{2-}) \quad (5.2)$$

$$(\text{Na}^+) = (\text{Bi}^{3+}) - (\text{Ta}^{5+}) + 3 (\text{Na}^+) \quad (5.3)$$

$$(\text{Ta}^{5+}) = (\text{Bi}^{3+}) - (\text{O}^{2-}) \quad (5.4)$$

$$(\text{Ta}^{5+}) = (\text{Bi}^{5+}) \quad (5.5)$$

$$(\text{Na}^+) + (\text{Ta}^{5+}) = 2 (\text{Bi}^{3+}) \quad (5.6)$$

Impurity-free XRD patterns and systematic increments in the unit cell volumes indicate that Bi has been accommodated in the lattice, irrespective of the synthesis conditions. The sample in the series S2 were prepared under Na-deficient conditions, where the number of moles of Na and Bi are equal to the number of moles of Ta ions ($M_{\text{Na}} + M_{\text{Bi}} = M_{\text{Ta}}$). Thus under this condition the occupancy of Bi at Na site together with cation vacancies is favorable according to equations 5.1 to 5.3. Similarly, samples in the series S1 were prepared under strongly Na-rich conditions, where $M_{\text{Na}} > M_{\text{Ta}} + M_{\text{Bi}}$. Thus the occupancy of Bi ions at Ta sites with the formation of oxygen vacancies is favorable according to equation 5.4. Alternatively substitution of Bi⁵⁺ at Ta⁵⁺ may also be possible as suggested by equation 5.5. The initial stoichiometry of the samples in the series S3 implies that occupancy of Bi

ions at both Na and Ta sites is likely to be favorable. In this case, the ionic charge neutrality in the lattice is maintained and thus the concentration of the native defects is likely to be minimal (equation 5.6). In order to understand the location of Bi ions in the lattice, detailed Rietveld refinements of the XRD patterns were carried out.

5.4 Rietveld refinements of XRD patterns

The results of the Rietveld refinements of the samples in series S1, S2, and S3 are presented in Table 5.2, 5.3, and 5.4 respectively. A systematic trend in site of occupancy values of Bi ions at Na and Ta sites was observed for the samples in series S1, S2, and S3 for a given bismuth concentration. The samples in the series S2 showed prominent occupancy of Bi ions at Na site, while the samples in the series S1 showed predominant occupancy of Bi ions at Ta site. The site occupancy values in the samples in the series S3 indicated that Bi ions occupied both Na and Ta sites approximately in equal proportion. The estimated site occupancies were in good agreement with the stoichiometry predicted by initial synthesis conditions. For 2.5% Bi doping, distinction in the site occupancy values was not prominent across the series S1, S2, and S3. This could be attributed to the prominent solubility of Bi ions at Na site for low concentrations of Bi doping. Earlier studies have shown that dopant site in the crystal structure of simple perovskites can be controlled by adjusting the stoichiometry of the initial reactants [119, 120]. The behavior of the unit cell volume thus originated from the different site occupancies of Bi ions in NaTaO₃ lattice and respective native point defects so produced. All the doped samples showed reduced crystallite size compared to that of the pristine NaTaO₃. The crystallite size decreased along with the

increase in bismuth content in each series, indicating that Bi doping does not promote grain growth. Further, the samples in the series S2 showed smallest crystallites sizes among all. It is known that excess amount of Na acts as flux and provides good crystallinity, thus under Na-deficient conditions, crystal growth was hampered [121]. All the doped samples showed increased strain values compared to the pristine structure indicating that Bi accommodation in the lattice has been occurred.

Table 5.2 The results of the Rietveld refinements of XRD patterns of samples in series S1

Series S1			
Sample	2.5%	5.0%	7.5%
Cell Volume (Å ³)	236.282 (73)	236.265 (73)	236.330 (93)
a (Å)	5.4904 (10)	5.4912 (99)	5.4905 (12)
b (Å)	5.5211 (91)	5.5205 (91)	5.5230 (12)
c (Å)	7.7947 (14)	7.7939 (15)	7.7934 (19)
Crystallite Size (nm)	228.4 (25)	146.74 (99)	118.78 (85)
Strain (%)	0.1969 (25)	0.2155 (27)	0.2010 (36)
Occupancy Bi (Na)	0.0057 (12)	0.0103 (10)	0.0147 (15)
Occupancy Bi (Ta)	0.0193 (12)	0.0397 (10)	0.0603 (15)
B _{Na} (Å ²)	1.150 (12)	1.361 (81)	1.491 (98)
B _{Ta} (Å ²)	0.435 (14)	0.388 (86)	0.243 (10)
R _{wp} (%)	5.36	6.15	5.12
R _{Bragg} (%)	2.086	1.484	1.677

Table 5.3 The results of the Rietveld refinements of XRD patterns of samples in series S2.

Series S2			
Sample	2.5%	5.0%	7.5%
Cell Volume (Å ³)	236.443 (16)	236.33 (82)	236.720 (24)
a (Å)	5.4997 9(20)	5.4952 (15)	5.5028 (30)
b (Å)	5.51834 (20)	5.5179 (10)	5.5236 (30)
c (Å)	7.7906 (36)	7.7975 (17)	7.7882 (51)
Crystallite Size (nm)	138.40 (11)	126.62 (28)	100.60 (11)
Strain (%)	0.2263 (42)	0.2271 (82)	0.2312 (82)
Occupancy Bi (Na)	0.0250 (13)	0.034 (11)	0.0582(26)
Occupancy Bi (Ta)	0.0000 (13)	0.016 (11)	0.0168(26)
B _{Na} (Å ²)	2.09 (12)	1.53 (67)	2.31 (16)
B _{Ta} (Å ²)	0.158 (13)	0.41 (73)	0.147 (20)
R _{wp} (%)	5.56	5.69	6.15
R _{Bragg} (%)	2.625	1.560	1.339

Table 5.4 The results of the Rietveld refinements of XRD patterns of samples in series S3.

Series S3			
Sample	2.5%	5.0%	7.5%
Cell Volume (Å ³)	236.301(86)	236.520 (13)	236.553 (13)
a (Å)	5.4906 (12)	5.4969 (18)	5.4963 (17)
b (Å)	5.5226 (11)	5.5237 (16)	5.5215 (16)
c (Å)	7.7929 (17)	7.7897 (28)	7.7948 (28)
Crystallite Size (nm)	166.10 (14)	124.50 (11)	111.76 (80)
Strain (%)	0.2288 (30)	0.2183 (46)	0.2248 (44)
Occupancy Bi (Na)	0.0118 (25)	0.0211 (14)	0.0225 (93)
Occupancy Bi (Ta)	0.0132 (25)	0.0289 (14)	0.0525 (93)

$B_{Na} (\text{\AA}^2)$	1.560 (11)	1.634 (12)	2.130 (10)
$B_{Ta} (\text{\AA}^2)$	0.204 (12)	0.125 (12)	0.244 (11)
$R_{wp} (\%)$	6.35	5.59	6.23
$R_{Bragg} (\%)$	1.658	1.954	1.435

Figure 5.6 (a) A representative Rietveld refined XRD pattern: (Red) fitted pattern (Blue) experimental pattern and (b) the ratio of intensity of 002 and 020 peaks in the XRD pattern of the samples in series S2 and S1 (5% Bi doping).

In the present Rietveld refinements, the total content of bismuth was constrained to the values of the starting stoichiometry. It was confirmed that a similar trend in the site occupancy values was obtained even for the unconstrained refinements. In the case of unconstrained refinements, the site occupancy values of the Bi ions did not match to the stoichiometry which was observed in the chemical analysis. This discrepancy was attributed to the differences in the x-ray scattering factors, crystal imperfections (point defects) present in the samples. Figure 5.6 (a) shows a representative fit between model pattern and experimentally recorded XRD pattern. All the refinements converged well with R_{bragg} values less than 3% and R_{wp} values (goodness of fit) less than 7%. Theoretically, a significant

contrast exists between the x-ray scattering factors of Bi³⁺ and Na¹⁺ ions and therefore, the occupancy of Bi at Na site is likely to change the intensities of certain peaks in the XRD pattern. The changes in these intensities were evident from the ratio of intensities of 002 and 020 peaks for the XRD patterns of S1 and S2 samples (Figure 5.6 (b)). The changes in the intensities of 002 and 020 peaks clearly indicate that Bi ions occupy Na sites under Na-deficient conditions.

Although the XRD patterns show lack of impurities of Bi₂O₃ or other phases, impurities may be present in minute concentrations which are not detected by powder X-ray diffraction technique. XRD technique fails to detect the phases if they present in extremely small concentrations or buried under other prominent phases [122]. Therefore, it is understood that for a bismuth concentration under consideration, all of Bi ions may not have been fully accommodated in the lattice. These impurities can be detected by other characterization techniques like Micro-Raman microscopy [123]. However, in the present samples the changes in the unit cell volumes and optical properties (explained later) suggest that doping of bismuth has taken place with increasing concentration up to 7.5% as the effects of doping on the optical and photocatalytic properties are found to be prominent. Therefore the even if the trace amounts of impurities were present in the samples, its effect, in the interest of the photocatalytic properties was considered in the present study.

5.5 Microstructure

Secondary electron micrographs of the pristine and 7.5% Bi doped NaTaO₃ powders are shown in figure 5.7 (lower magnification) and figure 5.8 (higher magnification). The pristine NaTaO₃ powders showed cuboid shaped particles with a large particle size variation, ranging between 200 to 800 nm (Figure 5.8-a). The particles in the series S1 were smaller in size as compared to that of the pristine NaTaO₃, ranging between 100 to 400 nm. These particles showed cuboid shapes with sharp edges (Figure 5.8-b). On the other hand, the particles in the series S2 showed agglomerated growth.

Figure 5.7 Scanning electron micrographs of (a) pristine NaTaO₃ and 7.5% Bi doped NaTaO₃ in series (b) S1, (c) S2, and (d) S3.

Figure 5.8 FESEM images of (a) pristine NaTaO₃ and 7.5% Bi doped NaTaO₃ in series (b) S1, (c) S2, and (d) S3.

These particles were no longer cuboids but rather irregular in shape and were larger in size as compared to the pristine NaTaO₃ (Figure 5.8-c). The particles in the series S3 showed sharp edges and facets with reduced particles size as compared to that of the pristine NaTaO₃. Prominent rectangular shapes and sharp facets were seen in the SEM observation of the particles in series S3 (Figure 5.8-d). The irregular and agglomerated growth of the samples in the series S2 indicated that the crystallinity of the powders was reduced. This result was consistent with the crystallite size values obtained from the XRD analysis. Further, the electron micrographs of the samples in the series S3 showed that increase in bismuth content caused sharp edges and facets in the particles which indicated that growth along certain directions was prominent under mildly Na-rich conditions (Figure 5.9).

Figure 5.9 FESEM images of samples in the series S3 with Bi doping of (a) 2.5%, (b) 5%, and (c) 7.5%.

Figure 5.10 Bright field TEM images of 7.5% Bi doped NaTaO₃ in S3 (a) bare catalyst surface (b) Platinum loaded catalyst surface.

Bright field images recorded using TEM were consistent with the FESEM observations (Figure 5.10). High resolution TEM images confirmed that nanoparticles of platinum (co-catalyst) were deposited on the surface of the catalyst and platinum deposition was uniform. Analysis of the phases based on the inter-planer distance (d), showed that platinum

nanoparticles were well crystalline and deposited on the crystalline facets of doped NaTaO₃ particles. Figure 5.11 shows the crystalline platinum with d-values of 3.9 Å corresponding to 100 planes of platinum. In addition, 113 planes of NaTaO₃ with d value of 2.14 Å is also evident in figure 5.11.

Figure 5.11 High resolution transmission electron micrograph of 0.06% platinum loaded 7.5% Bi doped NaTaO₃ showing crystalline phases of catalyst and co-catalysts.

5.6 Chemical analysis

In order to investigate the formal oxidation state and chemical environment of Bi ions in the doped samples, X-ray photoemission (XPS) spectroscopy analysis was carried out. All the doped samples showed presence of bismuth in XPS curves, irrespective of the synthesis conditions. A representative survey scan of 7.5% Bi doped sample in the series S2 is shown in figure 5.12. XPS spectra of Bi 4f, O 1s and Ta 4f were analyzed in the pristine and doped samples.

Figure 5.12 A representative XPS survey scan of 7.5% Bi doped NaTaO₃ in series S2 showing presence of Na, Ta, O and Bi peaks.

Figure 5.13 Fitting of the XPS spectra of Bi 4f in (a) pristine Bi₂O₃ and 5% Bi doped NaTaO₃ in series (b) S1, (c) S2, and (d) S3.

Figure 5.13 shows Bi 4f spectra of pristine Bi₂O₃ and 5% Bi doped NaTaO₃ samples. The peaks in XPS spectra at around 158.35 and 163.65 eV were assigned to Bi 4f_{7/2} and 4f_{5/2} in Bi³⁺ oxidation state [124]. There were no obvious higher energy components corresponding to Bi⁵⁺. Earlier studies on bismuth compounds have showed that Bi⁵⁺ peak appears at energy position which is around 2 eV higher than that of Bi³⁺ peak [125]. Thus the possibility of presence of Bi⁵⁺ was eliminated in the current study. The binding energy values of Bi 4f followed a trend i.e. S2 > S3 > S1 > Bi₂O₃ (Table 5.5). The pristine Bi₂O₃ showed single components for Bi 4f_{7/2} and 4f_{5/2} peaks. However, all the doped samples showed two components of the binding energy peaks which could be attributed to the presence of more

than one chemical environment. As mentioned earlier, under strongly Na-rich and Na-deficient conditions the occupancy of Bi ions at Ta and Na site was prominent, respectively. Thus the observed differences in the binding energies were attributed to differences in the chemical environment, i.e. location of Bi ions at different sites in the NaTaO₃ lattice. Tables 5.5, 5.6, and 5.7 show the carbon corrected binding energy values of Bi 4f, O 1s and Ta 4f orbitals respectively, in pristine Bi₂O₃ and Bi doped NaTaO₃ samples.

Table 5.5 Carbon corrected binding energy values (eV) of Bi 4f components in the pristine Bi₂O₃ and Bi doped NaTaO₃ samples.

Sample/BE (eV)	Bi 4f _{7/2}		Bi 4f _{5/2}	
Bi ₂ O ₃	158.350	--	163.650	--
S1	158.900	157.141	164.199	162.506
S2	159.335	158.107	164.635	163.407
S3	158.908	157.203	164.182	162.535

Table 5.6 Carbon corrected binding energy values (eV) O 1s components in pristine and Bi doped NaTaO₃.

Sample/BE (eV)	O 1s	O 1s
NaTaO ₃	529.232	531.306
S1	530.076	533.690
S2	530.381	533.810
S3	530.150	532.047

Table 5.7 Carbon corrected binding energy values (eV) of Ta 4f pristine and Bi doped NaTaO₃ samples.

Sample/BE (eV)	Ta 4f _{5/2}	Ta 4f _{7/2}
NaTaO ₃	27.310	25.440
S1	27.363	25.365
S2	27.643	25.686
S3	27.532	25.468

The binding energy values of O1s peaks in all the doped samples are greater than those in pristine NaTaO₃ (Table 5.6). Similar to Bi 4f peaks, the chemical shifts in the binding energy of O 1s spectra may be attributed to the replacement of Na-O and Ta-O bonds by Bi-O bonds in the doped samples. The trends in the binding energy values suggest that different chemical environments are present under different synthesis conditions. A similar trend was observed for other Bi doped NaTaO₃ samples in series S1, S2 and S3. Although quantitative analysis of the elements is possible by using XPS technique, the results obtained by XPS analysis are limited only to the surface of the samples. Therefore, to estimate the content of bismuth in the final products, samples were analyzed by Energy Dispersive Spectroscopy (EDS) method.

The compounds of bismuth are evaporative in nature at high temperatures. Thus to estimate the amount of bismuth in the final powders, samples were analyzed by Energy Dispersive Spectroscopy (EDS) technique. An average ratio of tantalum to bismuth in all the samples was recorded over five different readings. EDS analysis of the doped samples showed

presence of Na, Ta, Bi and O while no bismuth was found in the pristine NaTaO₃ sample. Table 5.8 shows the molar ratio of Ta/Bi for Bi doped samples in the series S1, S2, and S3. EDS analysis showed that irrespective of Na/Ta ratio used in the preparation of the samples, the content of Bismuth in the final products was close to that of the starting stoichiometry. A small loss of bismuth was attributed to the possible evaporative at high temperatures. Representative EDS plots of 7.5% Bi doped samples showing the presence of Bi (M), Ta (L), O (K) and Na (K) lines are shown in Figure 5.14. The XPS spectra and the EDS measurements showed that all the samples contain Bi³⁺ ions in Bi-O form and concentration of Bi ions in the final products was close to that of the initial values.

Table 5.8 Summary of EDS analysis showing molar ratio of Ta/Bi in doped samples.

Ta/Bi	S1	S2	S3
0.0	--	--	--
2.5	49.47	51.65	54.23
5.0	20.48	21.69	23.25
7.5	13.19	12.45	13.24

Figure 5.14 Energy dispersive spectra of 7.5% Bi doped NaTaO₃ samples in the series (a) S1, (b) S2, and (c) S3.

5.7 Optical properties

The changes in the synthesis conditions produced significant changes in the optical absorption properties of Bi doped samples. The diffused reflectance spectra of the samples in series S1, S2 and S3 are compared with that of the pristine NaTaO₃ in figure 5.15a-5.15c. The band gap value of the pristine NaTaO₃ was found to be 4.01 eV. The absorption spectra of all of the doped samples showed extension towards longer wavelengths along with

increase in Bi content, indicating that change in the optical absorption was caused by Bismuth doping. The band gap values of the samples estimated by Kubelka-Munk function are presented in Table 5.9. The absorption edge of samples in the series S1 (Figure 5.15a) was shifted towards the visible wavelengths and the band gap values were close to the visible region, except for 2.5% Bi doped sample. The poor absorption could be attributed to low concentration of bismuth. On the other hand, the absorption spectra of S2 samples (Figure 5.15b) did not show visible light absorption ($\lambda > 420$ nm).

Figure 5.15 Diffused reflectance spectra of Bi doped NaTaO₃ samples in the series (a) S1, (b) S2, and (c) S3 (x is the fraction of Bi doping).

The tail of the absorption spectra showed extension towards longer wavelengths, while the edge of the curve appeared around 300 nm. The estimated band gap values were in the UV region. Interestingly, the samples from the series S3 showed intense visible light absorption (Figure 5.15c) extending up to 550 nm. Similar to the S1 series, 2.5% Bi doped sample in S3 series showed poor absorption. The band gap values of the samples in the series S3 were lower than those of the samples in the series S1 and S2. The above results indicated that extent of the band gap narrowing was dependent on the initial stoichiometry of the starting materials as well as the bismuth content. Figure 5.16 shows the variation in the band gap values along with the bismuth content. It was observed that the band gap narrowing was not linear with the bismuth content. The band gap of 7.5% Bi doped sample in the series S3 was found to be the lowest (2.64 eV). The origin of the differences in the optical spectra is explained by the detailed study of the band structures of Bi doped NaTaO₃ in the next section.

Table 5.9 The band gap values of Bi doped NaTaO₃ samples obtained by Kubelka-Munk analysis.

Series / Bi Content (x)	S1 (eV)	S2 (eV)	S3 (eV)
0	4.01	4.01	4.01
0.025	3.65	3.75	3.85
0.05	3.05	3.65	2.77
0.075	2.95	3.65	2.64

Figure 5.16 Comparison of the band gap values of doped samples along with bismuth content in the series S1, S2, and S3.

5.8 Band structure calculation

The band structure calculations carried out to select the appropriate dopants were performed on NaTaO₃ space group No. 62, Pcmn, which is the most commonly studied phase. However, the present experiments resulted in the formation of NaTaO₃ which belonged to space group No. 62, Pbnm. It is worth noting that these symmetries arise from the different cell settings of the orthorhombic crystal structure. The polyhedral coordination and its connectivity remains the same in both the structures. The lattice parameters b (7.7952 Å) and c (5.4842 Å) of the phase Pcmn are close to those of c (7.7890 Å) and b (5.5212 Å) of the Pbnm. A small difference in the values of the parameters is observed between the two phases. To understand and explain the optical properties of experimentally synthesized

samples, the band structure calculations are carried out on NaTaO₃ with space group No. 62, Pbnm symmetry. Further, the experimental results showed that the synthesis conditions affected the substitution site of Bi in the lattice and thus changed the band gap values significantly. To understand the effect of Bi substitution at Na, Ta and both Na and Ta sites on the band structure, detailed electronic structures calculations on three different structures (Na_{1-x}Bi_xTaO₃, NaTa_{1-x}Bi_xO₃, Na_{1-x}Bi_xTa_{1-x}Bi_xO₃; x = 0.0625) were carried out. The results of these calculations are discussed in the following section.

Figure 5.17 Partial density of states of (a) NaTaO₃, (b) NaTa_{1-x}Bi_xO₃, (c) Na_{1-x}Bi_xTaO₃, and (d) Na_{1-x}Bi_xTa_{1-x}Bi_xO₃, x=0.0625.

The comparison of DOS of the pristine and Bi doped NaTaO₃ structures revealed that new energy states in between the band gap occurs on Bi doping. As shown in figure 5.17, the mid-gap energy states are responsible for a band gap reduction of 0.76 eV, 0.15 eV and 1.35 eV for the substitution of Bi at Ta site, Bi at Na site and Bi at both Na and Ta sites respectively. The site projected partial DOS shows that the substitution of Bi at Ta site induces energy states below the conduction band minimum (CBM) (Figure 5.18). These states are mainly composed of Bi 6s, O 2p, and Ta 5d orbitals, indicating that the electronic transition from O 2p to Bi 6s orbitals occurs during photoexcitation.

Figure 5.18 Partial density of states (PDOS) of NaTa_{1-x}Bi_xO₃ (x=0.0625)

On the other hand, the substitution of Bi at Na site creates new energy states above the valence band maximum (VBM). These states appear as a shoulder to the VB and they are formed by Bi 6s and O 2p orbitals (Figure 5.19). When Bi is substituted at both Na and Ta sites, extra energy states appear in between the band gap (Figure 5.20). These states are located at 0.80 eV above the VB and consist of Bi 6s, O 2p, and Ta 5d orbitals. For Bi substitution at Na site and at both Na and Ta sites, DOS analysis suggests that electronic transition from filled Bi 6s to empty Ta 5d orbitals takes place.

Figure 5.19 Partial density of states (PDOS) of Na_{1-x}Bi_xTaO₃ (x=0.0625).

In all cases, it is clear that the band gap narrowing is caused by the newly formed energy states derived from Bi 6s orbitals, indicating that bismuth accommodation in the lattice is the

cause of visible light absorption. It was noted that the results DOS plots of Bi doped NaTaO₃ structures with Pcmn and Pbnm symmetry did not differ significantly. Further, substitution of Bi at Na site introduces two excess negative charges. Thus the Fermi energy in this case is found to be present in CBM in DOS plots. However, to compare the dopant induced states in each case, the Fermi energy of all the samples was set to the VBM.

Figure 5.20 Partial density of states (PDOS) of Na_{1-x}Bi_xTa_{1-x}Bi_xO₃ (x=0.0625).

Although DOS analysis does not provide information about the absolute band edge potentials, the mechanism of band gap narrowing indicate the qualitative trends in the modification of the CB and VB. The band edge potentials of the photocatalyst play an important role in photooxidation and photoreduction reactions. For the photocatalytic water

splitting reaction, it is essential that the VB of the photocatalyst is more positive than the O₂/H₂O oxidation potential and the CB is more negative than H₂/H₂O reduction potential. In all the cases i.e. S1, S2, and S3, the mechanism of band gap narrowing is different, thus the band edge potentials are altered in different manner. Figure 5.21 shows the proposed band diagram of Bi doped NaTaO₃ structures. For substitution of Bi at Ta site the effective CB potential is shifted to more positive values. Upon visible light excitation, the electrons in CB have higher electrochemical potential and thus overpotential for hydrogen generation is reduced. On the contrary, replacing Na by Bi leaves the CB potential unchanged and the VB is slightly shifted towards negative potentials. Interestingly, for partial occupancies, the CB potential of samples is intact. Bi 6s induced energy states are completely filled and appear in between the band gap, thus the effective VB potential shifts towards lower values. The band edge potentials of these powders may prove favorable for the photocatalytic hydrogen generation.

Figure 5.21 Proposed band diagram of (a) pristine NaTaO₃, (b) NaTa_{1-x}Bi_xO₃, (c) Na_{1-x}Bi_xTaO₃, and (d) Na_{1-x}Bi_xTa_{1-x}Bi_xO₃ (x=0.0625).

5.9 Comparison of band gaps: DFT and experiments

The band gap values of Bi doped samples estimated by Kubelka-Munk analysis and those predicted by DFT calculations are in good agreement with each other. The decrease in the band gap values predicated by DFT calculations (0.15 eV for Bi at Na site, 1.35 eV for Bi at both Na and site, 0.76 eV for Bi at Ta site) follows the same trend as observed in the optical absorption spectra of the samples in the series S2, S3, and S1 respectively. Figure 5.22 shows the comparison between the band gap values obtained from the experimental samples (7.5% Bi doping) and DFT calculations (6.25% Bi doping). It is worth noting that the samples prepared in series S1, S2 and S3 do not have exact site occupancies as studied in the DFT calculations. Thus small amount of discrepancy is observed.

Figures 5.22 Comparison of the band gap values obtained from DRS spectroscopy and DFT calculations for 7.5% Bi doping.

It is further noted that the models studied by DFT calculations are perfect; however, Bi doped powders may not be homogeneous and thus may not represent the perfect structures. The occupancies of Bi ions in the experimental samples were found to be predominant at Na and Ta site while the DFT models assume complete substitution of Bi ions at cations sites. The point defects present in the structures are not accounted in the DOS calculations, while native point defects are expected to be present in samples. It is noted that the concentration and nature of these point defects experimentally unknown and therefore appropriate models for DFT cannot be generated. Earlier study on the point defects has shown that they have no effect on the band gap of NaTaO₃ [110]. Nonetheless, the present models are able to explain the experimental results of the optical and photocatalytic properties.

5.10 Photocatalytic degradation of Methylene Blue (MB)

The samples prepared under different conditions showed markedly different optical absorption properties. These samples were tested for the photocatalytic degradation of the commonly studied organic pollutant Methylene Blue (MB) (Chemical structure shown in figure 5.23). MB is a colored dye and it absorbs radiation in the visible region and undergoes degradation to lower compounds. However this process is slow and in presence of photocatalysts the process of degradation of MB is significantly enhanced. A complete degradation into mineralized MB compound is given by equation 5.7. However, complete degradation is an ideally desired process and in practice, various possible intermediates are formed which may not be completely mineralized. The typical absorption spectra of MB molecule show two prominent peaks at 662 nm and 290 nm (Figure 5.24). The peak around

290 nm corresponds to aromatic rings and peaks between 600 to 700 nm originate from conjugated- π system [28, 126].

Figure 5.23 Chemical structure of Methylene Blue (MB).

(5.7)

Figure 5.24 Typical absorption spectra of MB molecule showing two prominent peaks at 660 and 290 nm.

Figure 5.25 C/C_0 curve under dark condition for 5% Bi doped NaTaO₃ sample (C is the initial concentration and C_0 is concentration at time t; 20 ppm MB).

Under the dark conditions, in the presence of catalyst powders, no significant change in the concentration of MB was observed for any of the samples in the series S1, S2, and S3 (Figure 5.25). Negligible changes in the concentration implied that MB molecules did not react with catalyst particles or did not undergo significant adsorption on the surface of the particles. Figure 5.26 compares the degradation rates of MB for 5% Bi doped samples in the series S1, S2, and S3 under the visible radiation ($\lambda > 420$ nm). There was about 30% decrease of the initial concentration of MB, without any catalyst (blank test).

Figure 5.26 C/C_0 curves of MB degradation over 5% Bi doped samples in S1, S2, and S3 (C_0 is the initial concentration, C is concentration at time t ; $\lambda > 420$ nm; 20 ppm MB).

This reduction could be attributed to photolysis of MB, which is consistent with earlier reported results [127, 128]. The samples prepared under mildly Na-rich conditions (S3) showed the highest degradation rates among all. The degradation rate of pristine NaTaO₃ was similar to that of the photolysis of MB. The photocatalytic activities showed a clear gradation between the performances as follows, mildly Na-rich > strongly Na-rich > Na-deficient. Figure 5.27 shows UV-VIS absorption spectra of MB solution with S3 sample, exposed to the visible light (> 420 nm). Both the peaks of MB were systematically decreased with time, indicating a complete degradation occurred during this process. Further, no new peaks appeared along with the time, suggesting that the degradation led to formation of simple species.

Figure 5.27 UV-VIS absorption spectra of MB solution with 5% Bi doped samples in the series S3, showing decrease in the area along with time ($\lambda > 420$ nm; 20 ppm MB).

Figure 5.28 C/Co curves of MB degradation over 7.5% Bi doped samples in S1, S2, and S3 (C_0 is the initial concentration, C is concentration at time t; $\lambda > 420$ nm; 20 ppm MB).

Figure 5.28 shows the photodegradation of MB by 7.5% Bi doped samples in the series S1, S2, and S3. These samples showed a trend similar to 5% Bi doped samples in the respective

series. It was observed that for 7.5% Bi doping, MB degradation was faster as compared to 5% Bi doping in the series S3. Figure 5.29 shows the concentration of the MB after 4 hours of photocatalytic reaction. It is clear that doped samples perform better than the commercially available catalyst P25 and the pristine NaTaO₃ photocatalyst. Earlier research on MB degradation suggests that in aqueous solution (in presence of oxygen), MB molecules form various intermediates [129]. It is speculated that MB molecule oxidizes to sulfoxide (S=O). This is followed by breaking of the central aromatic ring which leads to the formation of complexes with one aromatic ring e.g. NH₂-C₆H₃-SO₃H-N-CH₃-COH or/and NH₂-C₆H₄- N-CH₃-CH₃. These complexes then dissociate into simpler compounds like phenol, C₆H₅-SO₃H and finally form carbon dioxide, water and acids. As mentioned earlier the peaks around 290 nm corresponds to the aromatic ring and this peak is systematically decreased in our experiments. Therefore it is concluded that the degradation of MB molecules to lower compounds has been occurred by photocatalysis.

The photocatalytic behavior of the samples was consistent with the optical absorption properties. The samples prepared under mildly Na-rich conditions showed higher amount of visible light absorption than other samples. The lower amount of absorption of visible light was the primary reason for the poor activities of S2 and S1 samples.

Figure 5.29 The concentration of MB after 4 hours of visible light irradiation over different samples ($\lambda > 420$ nm).

5.11 Photocatalytic hydrogen evolution

All the samples were tested for the photocatalytic hydrogen evolution in presence of the sacrificial agent under the irradiation of visible and UV i.e. UV-vis (250-800 nm) light. Figure 5.30 shows the rates of hydrogen evolution from 5% Bi doped samples under UV-vis irradiation. All the doped samples were active for H₂ evolution, while the samples in the series S1 showed the highest yield which was followed by those in series S3 and S2 respectively.

Figure 5.30 Photocatalytic hydrogen evolution from 5% Bi doped samples in the series S1, S2, and S3 under UV-vis radiation (250-800 nm) (20 mL CH₃OH, 80 mL D.I. water).

Figure 5.31 shows the hydrogen yield from 7.5% Bi doped samples in series S1, S2 and S3. The photocatalytic activity was significantly decreased compared to that of 5% Bi doped samples. However, the samples showed a behavior which was similar to the 5% Bi doped samples. It was clear that the doping of Bi ions reduced the photocatalytic activity under UV-vis radiation.

Figure 5.31 Photocatalytic hydrogen evolution from 7.5% Bi doped samples in the series S1, S2, and S3 under UV-vis radiation (250-800 nm) (20 mL CH₃OH, 80 mL D.I. water).

The samples in S1 were prepared under strongly Na-rich conditions. It is known that Na-rich conditions lead to suppression of Na vacancy and good crystallinity in the powders. The samples in S2 and S3 are prepared under mildly Na-rich and Na-deficient conditions respectively and thus these samples showed reduced crystallinity and were likely to have increased Na vacancy defects. Poor crystallinity and native point defects hamper the photocatalytic hydrogen evolution and therefore hydrogen evolution from S2 and S3 samples was lower than that of S1 samples. Further, all the doped samples showed lower hydrogen yield than that of the pristine NaTaO₃ and this is attributed to the reduced crystallinity and distortion in the lattice caused by Bi accommodation. The samples with 2.5% Bi doping from series S1, S2, and S3 did not differ significantly in the photocatalytic activity. Further, it was noted that the hydrogen evolution curves for 5% and 7.5% Bi doping

were not linear. This behavior indicates that structural changes in the photocatalyst surface such as peroxide formation, UV induced color centers, oxidation of the surface species may have occurred during first few hours.

When the samples were irradiated with visible light ($\lambda > 390$ nm), only traces of hydrogen were observed. Thus in order to enhance the electron-hole separation and increase the photocatalytic yield, platinum nanoparticles were loaded on the surface of the samples. The sample with the highest visible light absorption i.e. 7.5% Bi doped NaTaO₃ in series S3 was selected to find out the optimum amount of platinum. Figure 5.32 shows the effect of varying amount of platinum on the photocatalytic hydrogen evolution. The present data shows that hydrogen evolution increased with 0.03% (by wt.) of Pt loading compared to the bare photocatalyst surface. A maximum yield was obtained for 0.06% of platinum loading and thereafter it reduced to lower values. Excess loading of platinum nanoparticles blocks the light absorption as well as the active sites on the photocatalyst surface, thus at higher values i.e. 0.10% and 0.13% the samples showed reduced H₂ yield. Thus 0.06% of platinum was loaded on all of the doped samples in all the series.

Figure 5.32 The effect of platinum loading on the photocatalytic hydrogen evolution from 7.5% Bi doped NaTaO₃ samples in the series S3 (20 mL CH₃OH, 80 mL D.I. water; $\lambda > 390$ nm).

Figure 5.33 shows comparison H₂ evolution between 0.06% Pt loaded 7.5% Bi doped samples in the series S1, S2, and S3. It was seen that no significant amount of hydrogen was evolved from the samples in the series S1 and S2. Therefore it was concluded that Bi doped NaTaO₃ samples grown in the mildly Na-rich conditions (S3) were suitable for hydrogen generation. Within S3 series, the yield of hydrogen increased with increased Bi doping and was the maximum for 7.5% Bi doping ($0.86 \mu\text{mole h}^{-1}\cdot\text{g}^{-1}$) (Figure 7.34). It was confirmed that the hydrogen evolution is reproducible as well as consistent for multiple cycles. The photocatalytic activity of this catalyst was found to be stable up to 36 hours.

Figure 5.33 Comparison of the photocatalytic hydrogen evolution from 7.5% Bi doped NaTaO₃ samples in the series S1, S2, and S3 (20 mL CH₃OH, 80 mL D.I. water; $\lambda > 390$ nm).

Figure 5.34 The photocatalytic hydrogen evolution from samples in the series S3 with increasing Bi content (20 mL CH₃OH, 80 mL D.I. water; $\lambda > 390$ nm).

Both the photocatalytic tests i.e. MB degradation and hydrogen evolution showed that the samples in the series S3 had superior performance than those in the series S1 and S2. The photocatalytic behavior of the samples is explained in the following section. The samples in the series S3 showed intense visible light absorption and the estimated band gap values were lower than those of the samples in S1 and S2 series. The samples in the series S2 were prepared under Na-deficient conditions, which led to occupancy of Bi ions at Na site. The resulting crystal structure has lacked visible light absorption as shown by DRS spectra (and DFT calculations). The samples in the series S1 were prepared under strongly Na-rich conditions (Na/Ta ~ 1.1) and it was predicted that Bi ions predominantly occupy Ta site. Although this synthesis condition led to the band gap narrowing, the visible light absorption was limited compared to samples in S3. Higher the visible light absorption, more are the photoexcited charges available for photocatalytic reactions, thus the samples in the series S3 showed the superior performance.

Further, the band diagram of Bi doped NaTaO₃ structures indicated that the equal occupancy of Bi ions at both Na and Ta site was favorable for hydrogen evolution. The samples in S3 series (mildly Na-rich conditions) contained Bi ions at both Na and Ta sites and therefore possessed band edges suitable for hydrogen generation. DOS studies also showed that substitution of Bi at Ta site lowered the effective CB potential, thus samples in the series S1 possessed lower electrochemical potential for hydrogen generation than others. The lowering of CB potential may have contributed to loss of the photocatalytic hydrogen evolution. It is worth noting that dopant induced energy states (such as Bi 6s states below CB) are only significant when the sample is irradiated with visible light. Under the irradiation of UV-vis

light, the electrons are able to occupy the CB formed by Ta 5d orbitals (as in pristine NaTaO₃). Therefore under UV-visible radiation, the effective CB potential is not altered. This was evident from the photocatalytic activities under UV-visible irradiation.

Finally, doping of Bi³⁺ at cations sites in NaTaO₃ is an aliovalent type of doping. The occupancy Bi ions at Ta site would result in generation of oxygen vacancies while the occupancy Bi ions at Na site would result in the cation vacancies. However, the equal occupancy of Bi³⁺ ions at both Na and Ta sites helps maintain the ionic charge balance and thereby reduce the concentration of the native point defects. The native point defects act as electron-hole recombination centers and thus hamper the photocatalytic activity [23]. Therefore, due to the favorable band edge potentials, band gap, and ionic charge neutrality the samples in the series S3 showed higher photocatalytic activities than those in the other series under visible light irradiation.

Figure 5.35 compares the amount of hydrogen evolved from the samples in S3 series, after 12 hours of visible light irradiation. It is clear that Bi doped samples are active for visible light driven hydrogen evolution as compared to the pristine NaTaO₃.

Figure 5.35 The photocatalytic hydrogen evolution over Bi doped samples in S3 series after 12 hours of irradiation (20 mL CH₃OH, 80 mL D.I. water; $\lambda > 390$ nm).

5.12 Summary

Detailed investigations on Bi³⁺ doped NaTaO₃ powders were carried out using various experimental techniques as well as DFT based band structure calculations. It was shown that the optical properties of the doped powders can be tuned by tuning the synthesis conditions (Na/Ta ratio in the initial materials). A correlation between the synthesis conditions, crystal structure and the photocatalytic activity was established through a series of experiments. It was found that growth in mildly Na-rich conditions results in the maximum band gap narrowing on account of the occupancy of Bi ions at both Na and Ta sites. Further, optimum synthesis conditions (Na/Ta ratio, Bi content, and amount of co-catalyst) were estimated to achieve the visible light activity in the doped samples. Bi doped NaTaO₃ samples

demonstrated improved performance for Methylene Blue degradation over the commercial catalyst (Degussa-P25 (TiO₂)) under the visible light irradiation. In addition, platinum loaded Bi doped NaTaO₃ samples showed photocatalytic hydrogen evolution (0.86 $\mu\text{mole h}^{-1}\cdot\text{g}^{-1}$) in presence of methanol under visible light radiation.

Chapter VI: Bi doped NaTaO₃ - Hydrothermal Route

6.1 Introduction

This chapter presents the phase development, crystal structure and optical properties of Bi doped NaTaO₃ powders prepared by the hydrothermal route. The powders were tested for the photocatalytic hydrogen evolution under the visible light radiation ($\lambda > 390$ nm). The microstructure and photophysical properties of these samples are compared with those prepared by the solid state route.

The hydrothermal synthesis is a low temperature method to grow the crystalline materials. The nucleation and growth of the phase(s) of interest is facilitated in a Teflon lined autoclave under autogeneous pressure. This method is commonly used to prepare nanoparticles of the oxides with high surface area. The hydrothermal synthesis of alkali tantalates and titanates has been widely studied and the oxides prepared by these methods have shown high photocatalytic activities on account of the higher surface area [130-132]. Starting from the metal oxide (Ta₂O₅) and sodium hydroxide (NaOH) solution in the water, NaTaO₃ can be synthesized at temperatures as low as 200°C. In the present study, NaBiO₃ was used as precursor of bismuth to synthesize Bi doped NaTaO₃. The crystal structure and stoichiometry of NaBiO₃ shows that it contains Bi⁵⁺ ions within edge shared oxygen octahedra [133]. As the starting material contains Bi⁵⁺ ions, substitutional doping of Bi⁵⁺ in NaTaO₃ lattice could be possible by this synthesis method. In addition, as mentioned earlier, this method can also offer an advantage of the high surface area. Therefore, Bi doped

NaTaO₃ particles were synthesized by the hydrothermal route. The following section presents the results and discussion on the photophysical properties of Bi doped NaTaO₃ powders prepared by the hydrothermal route.

6.2 Crystal structure and phase development

Figure 6.1 shows XRD patterns of the pristine and Bi doped NaTaO₃ powders prepared by the hydrothermal method. XRD patterns of all the samples matched well with the reported pattern of NaTaO₃ (Space Group No 62. Pbnm). In addition to NaTaO₃, a small amount of un-reacted Ta₂O₅ impurity was observed. However, no other phase was detected in the XRD patterns. The unit cell volumes of Bi doped samples increased along with bismuth content up to 7.5% Bi doping and reached saturation at 10% Bi doping (Figure 6.2). A small amount of Bi₂O₃ precipitation was observed for 10% Bi doped sample. Systematic increments in the unit cell volume and impurity free XRD patterns indicated that Bi ions were accommodated in the lattice. The increment in the unit cell volume was consistent with the ionic radii of constituent ions i.e. Bi³⁺ > Ta⁵⁺ or (Bi⁵⁺ > Ta⁵⁺). The Vegard's law was followed for the lattice parameters a and b up to 7.5% Bi doping, while an abrupt variation in the parameter c was observed along with the bismuth content. Linear changes in the values of a and b suggested that Bi ions were uniformly doped in the lattice. It was confirmed that the XRD pattern of the starting material, NaBiO₃ belonged to the hydrated phase of NaBiO₃·2H₂O, (JPCDS No. 00-302-1161) and no peaks belonging to NaBiO₂ or Bi₂O₃ were present.

Figure 6.1 XRD patterns of (a) pristine NaTaO₃, (b) 2.5%, (c) 5.0%, (d) 7.5%, and (e) 10% Bi doped NaTaO₃ prepared with 6M NaOH.

Figure 6.2 The variation in the unit cell volumes along with bismuth content.

In order to understand the effect of NaOH concentration on the crystal structure of the final products, the samples were prepared with varying NaOH concentrations. Figure 6.3 shows the XRD patterns of 7.5% Bi doped samples with varying NaOH concentration. For higher concentrations of NaOH, i.e. 6M, NaTaO₃ and traces of un-reacted Ta₂O₅ were seen. As NaOH concentration decreased, the amount of un-reacted Ta₂O₅ increased. At lower concentrations (< 0.5 M), a pyrochlore structured Na₂Ta₂O₆ phase was formed along with NaTaO₃ and Ta₂O₅. It was observed that the growth of Na₂Ta₂O₆ phase was promoted at lower NaOH concentration. It was also observed that this phase was crystallized only when dopant precursor NaBiO₃ was present. In absence of NaBiO₃, at low NaOH concentrations only NaTaO₃ and Ta₂O₅ were formed. Lee and co-workers have showed that the selective synthesis of Na₂Ta₂O₆ and NaTaO₃ thin films can be successfully carried out by controlling NaOH concentration as well as temperature [134]. A similar phenomenon of formation of pyrochlore and perovskite type sodium tantalate was observed in the present work. Along with NaOH concentration, amount of bismuth precursor (NaBiO₃) was found to affect the phase formation. The two crystal structures of sodium tantalates differ in terms of their packing factors and lattice parameters. NaTaO₃ (Space group No. 62, Pcmn, Pbnm) is a close packed structure while Na₂Ta₂O₆ (Space group No. 227, Fd-3m) contains hexagonal interstitial tunnel framework. It is proposed that the nucleation of Na₂Ta₂O₆ phase may have occurred from Na-Bi-O complex in the solution. NaBiO₃·2H₂O has a layered type crystal structure and thus may have led to the formation Na₂Ta₂O₆ phase. In absence of NaBiO₃, Na-Ta-O complex is formed which leads to the formation of NaTaO₃. The pyrochlore type Na₂Ta₂O₆ is known to be a photocatalyst for the water splitting reaction (band gap 4.6 eV); However the photocatalytic activity of Na₂Ta₂O₆ is less than that of NaTaO₃ under UV radiation [10, 135]. Therefore, although pyrochlore phase (Na₂Ta₂O₆) was formed in the

present experiments, the investigations were focused on the photophysical properties of the perovskite phase (NaTaO₃). The earlier study has showed that higher NaOH concentration improved the crystallinity of the NaTaO₃ powders in the hydrothermal synthesis [130]. Therefore Bi doped NaTaO₃ powders were prepared with 6M NaOH solution and their optical and photocatalytic properties were investigated. The experimental measurements confirmed that the changes in NaOH concentrations (2-6 M) did not change the optical properties of the samples for any of the doped NaTaO₃ systems significantly.

Figure 6.3 XRD patterns of 7.5% Bi doped NaTaO₃ powders with (a) 6 M, (b) 2 M, (c) 0.5 M, and (d) 0.1 M of NaOH concentration.

Table 6.1 presents the results of the Rietveld refinements of the XRD patterns. These results showed that the crystallite size decreased and the strain increased along with Bi content. The average crystallite sizes of the samples prepared by the hydrothermal method were smaller

than those prepared by the solid state synthesis. The increment in the strain was consistent with the accommodation of higher content of Bismuth in the lattice. The site occupancy analysis showed that majority of Bi ions was situated at Na site while the remaining was present at Ta site.

It is widely accepted that the formation of oxides in the hydrothermal method occurs via dissolution-crystallization mechanism [136]. Complex species of Na-Ta-O are formed during the synthesis and these complexes subsequently crystallized into lower stoichiometric oxides as the temperature of the systems rises. In the present hydrothermal synthesis, extremely Na-rich synthesis conditions were maintained (Ta:Na ~ 1:20). It is noted that high concentration of NaOH was essential to breakdown Ta₂O₅ and thus to complete the chemical reaction. Therefore even though strongly Na-rich conditions were used to synthesize Bi doped NaTaO₃, the occupancy of Bi ions at Ta site was not observed. Unlike the solid state route, Bi doping in NaTaO₃ lattice did not occur by temperature induced diffusion process in the hydrothermal method. Thus the ratio of Na/Ta in the hydrothermal synthesis is not significant in controlling the site occupancy of Bi ions in the lattice.

Table 6.1 The Rietveld refinement results of XRD patterns of pristine and Bi doped NaTaO₃ samples prepared by hydrothermal method.

Sample	NaTaO ₃	2.5% Bi	5% Bi	7.5% Bi	10% Bi
Cell Volume (Å ³)	237.142(76)	237.492 (11)	237.677(11)	237.924(15)	237.933(12)
a (Å)	5.4959 (10)	5.5013 (14)	5.5028 (14)	5.5071 (21)	5.5057 (16)
b (Å)	5.5283 (10)	5.5296 (14)	5.5296 (14)	5.5338 (21)	5.5327 (15)
c (Å)	7.8049 (14)	7.8071 (23)	7.8102 (22)	7.8065 (37)	7.8109 (25)
Crystallite Size (nm)	168.4(30)	101.64 (61)	110.99 (75)	101.21 (76)	118.20 (89)
Strain (%)	0.1507(33)	0.2419 (40)	0.2419(40)	0.26713(37)	0.2400(42)
Occupancy Bi (Na)	--	0.0177(13)	0.0312(16)	0.0359(10)	0.0332(15)
Occupancy Bi (Ta)	--	0.0073(13)	0.0188(16)	0.03406(15)	0.0668(15)
B _{Na} (Å ²)	0.517(50)	1.592(94)	1.904(86)	2.262(98)	2.12(10)
B _{Ta} (Å ²)	0.189(10)	0.439 (90)	0.204 (96)	0.090 (12)	0.417 (11)
R _{wp} (%)	5.346	5.540	5.704	6.175	6.017
R _{Bragg} (%)	1.697	1.121	1.657	1.410	1.172

It was observed that the unit cell volumes of Bi doped NaTaO₃ samples were significantly increased. Theoretically Bi⁵⁺ substitution at Ta⁵⁺ (7.5%) would lead to an increment of 0.18 Å³. However, the present unit cell volumes showed that for 7.5% Bi doping the cell was expanded by 0.78 Å³, which is markedly larger than the theoretical prediction. Further, substitution of Bi⁵⁺ at Ta⁵⁺ maintains the ionic charge balance and thus this type of doping does not produce native point defects. Thus it is evident that cell volume changes arise from, doping of Bi³⁺ in NaTaO₃ lattice. This prediction is consistent with the XPS analysis (explained later).

6.3 Microstructure

Figure 6.4 (a) Bright field image, (b) High resolution transmission electron micrograph, and (c) selected area diffraction pattern of 7.5% Bi doped NaTaO₃ powders.

Figure 6.4 shows TEM images and selected area diffraction pattern of 7.5% Bi doped NaTaO₃ particles. The electron microscope images showed that the average particles size of the samples prepared by the hydrothermal method was smaller than those prepared by the solid state route (Figure 6.4-a). The selected area diffraction pattern corresponding to HRTEM (shown in figure 6.4-b) was indexed to 010 and 100 planes and conformed to orthorhombic NaTaO₃ phase (Figure 6.4-c).

Figure 6.5 FESEM images showing the surface of 7.5% Bi doped NaTaO₃ powders.

The morphology and surface of the particles is shown in Figure 6.5. The cuboid particles with prominently faceted surfaces were observed. Figure 6.6 shows the bright field image of platinum loaded Bi doped NaTaO₃ particles. The dark spots refer to platinum nanoparticles (0.15% wt.), indicating that platinum nano-particles were uniformly loaded on the surface of the catalyst.

Figure 6.6 Bright field image of 0.15% platinum nanoparticles loaded 7.5% Bi doped NaTaO₃ surface.

6.4 Chemical analysis and optical properties

To understand the oxidation states of bismuth in the final products, the XPS spectra of the samples was recorded. Figure 6.7 shows Bi 4f peaks in XPS spectra belonging to starting precursor NaBiO₃ and Bi doped NaTaO₃ powders. The doublet peaks in pristine NaBiO₃ was assigned to Bi³⁺ oxidation state (Figure 6.7-d). Although the stoichiometric phase (NaBiO₃·2H₂O) was confirmed by the XRD analysis, the formal oxidation state of bismuth

was found to be 3+. A similar phenomenon has been observed in earlier studies [125]. Bi⁵⁺ is considered as a metastable state and a possible redistribution of Bi ions in the lattice may have occurred while maintaining the crystal structure of the NaBiO₃ same. Figures 6.7a-6.7c show the XPS spectra of Bi doped samples with increasing Bi content. All the doped samples showed the presence of bismuth and Bi 4f peaks could be assigned to Bi³⁺ ions. It is known that NaBiO₃ is unstable and dissociates when exposed to moisture and heat. Earlier studies on NaBiO₃ have shown that NaBiO₃ undergoes phase transitions to the compounds with lower oxidation states when heated at higher temperatures (> 80°C) [137].

Figure 6.7 XPS spectra of Bi 4f peaks in Bi doped NaTaO₃ (a) 2.5%, (b) 5.0%, (c) 7.5%, and (d) pristine NaBiO₃.

In the present experiments, the hydrothermal treatment was carried out at 250°C in aqueous media. This temperature is sufficient to transform NaBiO₃ into Bi₂O₃ and other oxides containing lower oxidation states of bismuth. The XPS measurements and the unit cell volume expansions thus showed Bismuth was present in Bi³⁺ form in all the final products. The samples were also studied by EDS technique. It was confirmed that bismuth was present in each case and its concentration was close to the initial stoichiometry.

Figure 6.8 Diffused reflectance spectra of Bi doped NaTaO₃ samples prepared by the hydrothermal method. Inset showing the band gap values as function of Bi content.

The optical absorption spectra of the doped samples showed extension in the visible region (Figure 6.8). The absorption in the visible region was increased with the increase in bismuth content. The absorption spectra of 7.5% and 10% Bi doped sample did not differ significantly, which was consistent with the changes in the crystal structure (unit cell volumes) as indicated by the XRD patterns. The DRS spectra showed that Bi doping by the

hydrothermal method also enables the visible light absorption in NaTaO₃ powders. The band gaps of the samples calculated by K-M analysis were in the range of 2.95 – 3.25 eV. The inset in Figure 6.8 shows the variation of the band gap values with bismuth doping. The band structure calculations showed that occupancy of Bi ions at both Na and Ta sites in equal proportion led to intense visible light absorption. In the case of hydrothermally grown samples, XRD analysis revealed that the Bi ions are located at both Na and Ta sites; however, the occupancy at Na site is higher than that of Ta site. Thus it is proposed that due to the absence of equal occupancy of Bi ions at Na and Ta sites, the optical absorption of the hydrothermally grown samples was limited only to 450 nm.

6.5 Surface area

The surface area of the samples prepared by the hydrothermal route was found to be higher than those of the solid state counterparts. The adsorption-desorption curves of the samples prepared by the hydrothermal route showed a hysteresis which indicated a small amount of residual porosity. The estimated surface area of the pristine and doped samples prepared by both the routes are listed in Table 6.2. The surface area of the hydrothermally prepared samples was almost twice as that of the solid state counterparts. Further, it was evident that the bismuth doping as well as synthesis conditions had no significant effect on the surface area.

Table 6.2 Estimated surface area of Bi doped NaTaO₃ samples.

Sample	Surface Area (m ² g)
Solid State Synthesis	
NaTaO ₃	0.85
S1 - 5 % Bi	1.15
S2 - 5% Bi	1.02
S3 - 5% Bi	1.12
Hydrothermal Synthesis	
2.5% Bi	2.15
5.0% Bi	2.26
7.5% Bi	2.21

6.6 Photocatalytic hydrogen evolution

The samples prepared by the hydrothermal method were tested for the photocatalytic hydrogen evolution in presence of methanol. Negligible amount of hydrogen evolved from the bare surface of Bi doped powders under the visible light irradiation ($\lambda > 390$ nm). To enhance the hydrogen evolution by electron-hole separation, platinum nanoparticles were deposited on the photocatalysts surface.

Figure 6.9 Photocatalytic hydrogen evolution from 7.5% Bi doped NaTaO₃ with varying platinum content (20 mL CH₃OH, 80 mL D.I. water; $\lambda > 390$ nm).

Figure 6.9 shows the photocatalytic hydrogen evolution under visible radiation (> 390 nm) with the variation in platinum loading on the surface of 7.5% Bi doped NaTaO₃. The highest photocatalytic hydrogen evolution was observed for 0.15% loading (by wt.) of platinum. Thus same amount of platinum (0.15%) was loaded on the surface of other doped samples. It was observed that similar to the solid state samples, hydrogen yield increased with the increase in Bi content and for 7.5% Bi doped samples, a maximum hydrogen evolution rate of $0.72 \mu\text{·moles·h}^{-1}\cdot\text{g}^{-1}$ was obtained (Figure 6.10).

Figure 6.10 Photocatalytic hydrogen evolution from 0.15% Pt loaded Bi doped NaTaO₃ with increasing Bi content (20 mL CH₃OH, 80 mL D.I. water; $\lambda > 390$ nm).

No hydrogen was evolved from 10% Bi doped NaTaO₃ sample, indicating that 10% Bi doped sample contained markedly different photophysical properties from the other samples in the series. The site occupancy values obtained from Rietveld refinements showed that majority of Bi ions was located at Ta site in this sample. This could be the possible reasons of loss of photocatalytic activity in 10% Bi doped sample. A brief comparison of the samples prepared by two different methods is presented in section 6.7.

6.7 Comparison between solid state and hydrothermal route

Both pristine and Bi doped samples prepared by the hydrothermal route showed increased unit cell volumes than those prepared by the solid state route. The increased cell volume was attributed to the incorporation of OH⁻ ions in the lattice as the samples were prepared in presence of strong NaOH (6M) solution. Earlier research has shown that synthesis of perovskites like BaTiO₃, KNbO₃ in hydroxide media leads to the trapping of OH⁻ ions in the lattice thereby increasing the unit cell volumes [138, 139]. These OH⁻ ions were present inside the lattice thus washing of the samples had negligible effect on the unit cell volumes.

The yield of photocatalytic hydrogen evolution of 7.5% Bi doped samples prepared by the solid state (series S3) and hydrothermal route were comparable. However, the solid state sample showed slightly higher hydrogen evolution rate than its hydrothermal counterpart. The XRD patterns and BET measurements showed that the samples prepared by the solid state route have higher degree of crystallinity and lower surface area than those prepared by the hydrothermal route. Due to the higher surface area, hydrothermally prepared Bi doped samples had more active sites for the photocatalytic reactions. However, the absorption of the visible light by the hydrothermal samples was limited only up to 450 nm. Therefore in spite of the high surface area, the hydrogen evolution rate was found to be slightly lower than the solid state samples. The visible light absorption in the samples prepared by the solid state route was due to the equal occupancy of Bi ions at Na and Ta sites. It was observed that the occupancy of Bi ions in the lattice could not be tuned by the hydrothermal route. The

hydrothermal route follows dissolution-crystallization mechanism while the solid state route uses high temperature diffusion to form pristine and doped NaTaO₃.

6.8 Summary

Visible light active powders of Bi doped NaTaO₃ photocatalyst were prepared by low temperature hydrothermal route. The doped samples were active for the visible light driven hydrogen evolution in presence of methanol (A maximum yield of 0.7 $\mu\text{moles}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ for 7.5% Bi doping). The powders so prepared offered an advantage of higher surface area on account of nano-sized particles which was beneficial for the photocatalytic activity. The optical absorption properties of these powders could not be tuned by the synthesis conditions and visible light absorption was limited to 450 nm due to the inability to achieve equal site occupancy of Bi ions at Na and Ta sites in the lattice. Therefore, although the samples had high surface area, on account of the limited visible absorption, the samples showed lower hydrogen evolution rates than the solid state counterparts.

Chapter VII: Fe and La-Fe co-doped NaTaO₃

7.1 Introduction

The crystal structure, surface morphology and optical properties of Fe and La-Fe co-doped NaTaO₃ powders are discussed in this chapter in detail. The photocatalytic performance of the powders under visible ($\lambda > 390$ nm) and UV-vis (250-800 nm) irradiation, with and without co-catalyst loading is investigated. By establishing the co-relation between the crystal structure and the photocatalytic activity the photocatalytic behavior of the samples is explained.

The computational results in chapter IV showed that 3d transition metal ions are useful in reducing the effective band gap value of NaTaO₃. Among these metals ions, Iron (Fe) was selected as a potential dopant because Fe doping reduces the band gap of NaTaO₃ by 0.93 eV and Fe doped NaTaO₃ systems can be extended to co-doping of La and Fe. NaTaO₃ with Pbnm type space group presents a possibility of solid solution of LaFeO₃ and NaTaO₃ when La and Fe are co-doped together. The formation of the solid solution could be beneficial for the photocatalytic activity as it overcomes the drawbacks of aliovalent doping. Earlier studies have shown that the solid solutions such as ZnS-CdS [62] and GaN-ZnO [67] demonstrate promising photocatalytic activities in the visible region as compared to the aliovalent doping. The other (3d) transition metals such as Cr, Mn, and Co have shown similar trends in the band gap narrowing. However, co-doping of these ions with La do not offer an advantage because the respective lanthanum compounds, LaCrO₃, LaMnO₃,

LaCoO₃ crystallize in space groups other than that of NaTaO₃ (Pbnm). Further, the lattice parameters of LaFeO₃ and that of NaTaO₃ are significantly close to each other [140]. Thus due to its unique ability to form solid solution, La-Fe co-doping is worth investigating and holds a promise to develop the visible light photocatalysts. Fe³⁺ has ionic radii of 0.65 Å for VI oxygen coordination which is similar to the ionic radii Ta⁵⁺ 0.64 Å [115]. In addition, the electronegativity values of Fe (1.83) and Ta (1.50) are similar which indicates, that doping of Fe ions at Ta site is experimentally feasible. Therefore in the present study, photophysical properties of two different systems i.e. Fe doped NaTaO₃ and La-Fe co-doped NaTaO₃ were investigated. Fe doped NaTaO₃ powders with 2, 4, 6, and 8% Fe content are studied. In the case of co-doping, the samples are synthesized with each 2%Fe-2%La, 4% Fe-4%La, and 6%Fe-6%La which are referred to as 2%La-Fe, 4%La-Fe, and 6%La-Fe respectively. Additionally, La-doped NaTaO₃ samples were also prepared and characterized for comparison.

7.2 Crystal structure

Figure 7.1 shows the XRD patterns of Fe doped NaTaO₃ with increasing Fe content. All the XRD patterns showed the presence of a monophase and belonged to the crystal structure of pristine NaTaO₃ (space group No. 62, Pbnm) [95]. The unit cell volumes obtained from the Rietveld refinement of the XRD patterns are shown in Figure 7.2. The cell volume initially increased linearly up to 6% Fe doping and decreased for later values, suggesting that structural changes occurred after 6% Fe doping. As the cell volumes showed linear behavior up to 6% doping, this study was limited to Fe content up to 6%. This concentration of

doping was also comparable with computational studies. Systematic increment in the unit cell volumes and impurity free XRD patterns indicated that Fe ions were incorporated into the lattice successfully. The Rietveld refinements of XRD patterns showed that the crystallite size decreased and strain values increased along with Fe content (Appendix A). Further, the site occupancy values of Fe ions indicated that, Fe ions were predominantly substituted at Ta site, for Fe doping less than 8%.

Figure 7.1 XRD patterns (a) pure and (b) 2%, (c) 4%, (d) 6%, and (e) 8% Fe doped NaTaO₃ showing presence of monophasic.

Figure 7.2 Variation of unit cell volumes of Fe doped NaTaO₃ along with Fe content.

Figure 7.3 XRD patterns (a) pure and (b) 2%, (c) 4%, and (d) 6% (each) La and Fe co-doped NaTaO₃ showing presence of monophasic.

Figure 7.4 Expansion of the unit cell volumes of La-Fe co-doped NaTaO₃ along with dopant content.

Figure 7.3 shows the XRD patterns of La and Fe co-doped NaTaO₃. Similar to the Fe doping, all the XRD patterns showed the presence of monophasic (SG No. 62, Pbnm). The analysis of the XRD patterns showed that the increment in the cell volumes was significantly higher than that of the Fe doped samples (Figure 7.4). Accommodation of La and Fe was successful in the lattice as no impurities of Fe₂O₃ or La₂O₃ were seen in the XRD patterns. The reported unit cell volume of NaTaO₃ ($V=235.53 \text{ Å}^3$, $a=5.4768 \text{ Å}$, $b=5.5212 \text{ Å}$, $c=7.789 \text{ Å}$) [95] is smaller than that of LaFeO₃ ($V=242.92 \text{ Å}^3$, $a=5.55702 \text{ Å}$, $b=5.56521 \text{ Å}$, $c=7.85426 \text{ Å}$) [140] therefore it is expected that the addition of LaFeO₃ to NaTaO₃ would increase the cell volume. Table 7.1 lists the unit cell volumes of Fe doped, La doped and La-Fe co-doped samples.

Table 7.1 The unit cell volumes of doped and co-doped NaTaO₃.

System	Unit cell volume (Å ³)
NaTaO ₃	236.012
2% Fe - NaTaO ₃	236.121
2% La - NaTaO ₃	236.334
1% La-Fe - NaTaO ₃	236.651

7.3 Crystal defects

The substitutional doping of Fe³⁺ in NaTaO₃ is an aliovalent doping and may induce native point defects to maintain the ionic charge balance. The replacement of Ta⁵⁺ by Fe³⁺ would result in one vacancy of oxygen while replacement of Na¹⁺ by Fe³⁺ would result in certain cation vacancies. The possible charge compensation reactions are expressed by equation 7.1 to 7.5. Thus similar to the case of Bi³⁺ doping, the changes in the cell volumes were attributed to Fe³⁺ and La³⁺ accommodation in the lattice as well as native point defects so produced.

$$(\text{Fe}^{3+}) = (\text{Ta}^{5+}) + (\text{V}_\text{O}) \quad (7.1)$$

$$2 (\text{Fe})^{3+} = (\text{Ta}^{5+}) + (\text{Na}^{1+}) \quad (7.2)$$

$$(\text{Fe}^{3+}) = 2 (\text{V}_\text{Na}) \quad (7.3)$$

$$(\text{La}^{3+}) = 2 (\text{V}_\text{Na}) \quad (7.4)$$

$$(\text{Fe}^{3+}) + (\text{La}^{3+}) = (\text{Ta}^{5+}) + (\text{Na}^{1+}) \quad (7.5)$$

In the case of co-doping, it is noted that the occupancy of Fe³⁺ at Ta⁵⁺ site and occupancy of La³⁺ at Na¹⁺ site in equal proportion maintains the ionic charge balance in the lattice. Although equal occupancy of Fe³⁺ at both Na and Ta sites could achieve a similar charge balance, such occupancy is unlikely under present synthesis conditions. Fe doped samples were prepared under strongly Na-rich conditions. Moreover, the ionic radii of Fe³⁺ or Fe²⁺ (XII) and Na¹⁺ (XII) are significantly different which restricts the occupancy of Fe ions at Na site at least for low concentrations of doping (< 8%). The Rietveld refinements have shown that Fe ions predominantly occupy Ta site.

7.4 Optical properties and microstructure

The optical absorption spectra of the pristine and Fe doped samples are shown in figure 7.5. All the doped samples showed extension in the visible region compared to the pristine NaTaO₃. A peak prominent at around 500 nm appeared in all Fe doped samples. It was observed that the band gap narrowing increased with Fe content and for 6% Fe doping a band gap value of 2.34 eV was obtained as estimated by K-M plots. The band gap values reached saturation for higher Fe content and these results of higher Fe content were not included in the present study.

Figure 7.5 Diffused reflectance spectra of the pristine and Fe doped NaTaO₃ samples showing intense absorption in the visible region.

Figure 7.6 Diffused reflectance spectra of the pristine and La-Fe co-doped NaTaO₃ samples showing extension in the visible regions.

Similar to Fe doped samples, the absorption spectra of La-Fe co-doped samples showed shifts towards the visible region (Figure 7.6). However, unlike Fe doping, the absorption was limited to 550 nm and absorbance in the visible region was lower than that of Fe doped samples. A peak around 450 nm was observed in absorption spectra of co-doped samples.

Figure 7.7 shows the FESEM images of Fe doped NaTaO₃ powders. The surface of the doped powders did not show any significant facets. The shapes of the particles were deviated from perfect cuboid shape suggesting that crystallinity of the powders may be decreased with Fe doping.

Figure 7.7 Scanning electron micrographs of (a) 2%, (b) 4%, (c) 6%, and (d) 8% Fe doped NaTaO₃ powders showing powder surface.

Figure 7.8 Field emission scanning electron microscope images of (a) pristine, (b) 2%, (c) 4%, and (d) 6% La-Fe co-doped NaTaO₃ powders showing surface nano-steps.

On the other hand, as seen in figure 7.8, surface ‘nanosteps’ were observed for all La-Fe co-doped samples. It was found that the prominence of surface ‘nanosteps’ increased with increase in the doping concentration. It was also observed that the size of these steps was increased with the dopants content. For 6% La-Fe co-doping, the surface steps could be seen at lower magnification. The particle shape was found to be deviated from perfect cuboids as compared to that of the pristine NaTaO₃.

Figure 7.9 Exploded view of surface nanosteps on 2% La-Fe co-doped NaTaO₃.

Figure 7.10 Bright field images of the surface structure of 2% La-Fe doped NaTaO₃

Both FESEM and TEM observations confirmed that these steps were of the order of 20-50 nm (Figure 7.9 and Figure 7.10). It is worth noting that the surface nanosteps were not present in the pristine or Fe doped samples, while they were only seen in La-Fe co-doped powders. The characteristics surface nanosteps were first observed by Kudo et al. in lanthanide (La, Ce, Pr) doped NaTaO₃ systems [86]. Therefore in the present study it is clear that addition of La modifies the surface structure of the photocatalyst.

7.5 Band structure calculations

In order to understand the changes in the optical absorption spectra of the samples, the band structure calculations were carried out on Na_{1-x}La_xTaO₃, NaTa_{1-x}Fe_xO₃, and Na_{1-x}La_xTa_{1-x}Fe_xO₃ structures for $x=0.0625$. It is noted that the earlier calculations were carried out on NaTaO₃ structure belonging to Pcmn space group while the present calculations are done on NaTaO₃ with Pbnm space group, which was obtained in the experiments. By analyzing the DOS of these systems, the effect of La, Fe and both La and Fe co-doping on the band structures of NaTaO₃ was investigated. The total and site projected partial DOS plots of Na_{1-x}La_xTaO₃ are presented in figure 7.11.

Figure 7.11 Site projected partial density of states (DOS) of Na_{1-x}La_xTaO₃ ($x=0.0625$) (The dashed line represents the Fermi energy).

It is observed that doping of La at Na site leads to an increase in the band gap value by a 0.10 eV and the analysis of DOS plots shows that La doping does not induce any mid gap energy states. Figure 7.12 shows the total and site projected density of states (DOS) of NaTa_{1-x}Fe_xO₃ structure. The comparison of this result with the DOS of the pristine NaTaO₃ reveals that substitution of Fe at Ta site produces extra energy states in the band gap. The site projected DOS analysis shows that these gap states are mainly composed of Fe (3d) and O (2p) orbitals and are partially filled. In addition to these mid-gap states, Fe 3d induced states also appear at the bottom of the CB. These energy states reduce the effective band gap value of NaTaO₃ by 0.93 eV.

Figure 7.12 Site projected partial density of states (DOS) of NaTa_{1-x}Fe_xO₃ (x=0.0625) (The dashed line represents the Fermi energy).

Figure 7.13 shows the total and site projected DOS of Na_{1-x}La_xTa_{1-x}Fe_xO₃ structure. The substitution of La at Na site and Fe at Ta site creates mid gap energy states. As compared to the DOS of Fe doping alone, these mid gap states are shifted towards the CB and they are completely filled. The site projected DOS analysis confirms that these states are mainly formed by Fe (3d) and O (2p) orbitals. Further, it is also seen that in the case of co-doping the CBM is composed of Ta 5d induced energy states. The contribution of La orbitals in these mid gap states is found to be insignificant. These extra states are responsible for the effective band gap reduction of 1.23 eV.

Figure 7.13 Site projected partial density of states (DOS) of Na_{1-x}La_xTa_{1-x}Fe_xO₃, (x=0.0625) (The dashed line represents the Fermi energy).

The DOS analysis shows that in both the cases, Fe 3d deduced electronic states are responsible for the band gap narrowing and thus subsequent visible light absorption. The earlier studies on La doped NaTaO₃ have shown that La doping at Na site do not contribute to the mid gap states and do not alter the band gap significantly [113]. Our calculations are consistent with this result. Therefore it is clear that in the case of co-doping, the band structure is altered by Fe ions alone. The computational results and experimental absorption spectra confirmed that Fe doping in NaTaO₃ causes the visible light absorption. The computational results indicate that doping of Fe and co-doping of La and Fe would reduce the effective band gap of NaTaO₃ by 0.93 eV and 1.23 eV respectively. However, the experimental measurements do not show this trend. 6% Fe doped NaTaO₃ samples has a band gap of 2.34 eV, while the DFT calculations predict the band gap value to be 3.08 eV. It is understood that further investigation are needed to explain the trend in the optical absorption spectra. Spin polarized DFT calculations of Fe and La-Fe doped NaTaO₃, calculations on the crystal structures with varying distant between co-dopants (La-Fe) could possibly explain this discrepancy.

7.6 Photocatalytic hydrogen evolution

Figure 7.14 shows the hydrogen evolution curves of 2, 4, and 6% Fe doped NaTaO₃ and 2% La doped NaTaO₃ obtained under UV-vis (250-800 nm) irradiation. It is seen that 2% La doped NaTaO₃ showed the higher yield than that of the pristine NaTaO₃. This result was in good agreement with earlier studies, which state that small amount (~2%) of La addition enhances the photocatalytic activity of NaTaO₃ [79, 141]. Fe doped samples were found to be active for the hydrogen evolution under UV-vis radiation, however, all the samples showed lower yield of hydrogen than the pristine NaTaO₃ and 2% La doped NaTaO₃. Figure 7.15 shows the hydrogen evolution from La-Fe co-doped samples under UV-vis radiation in presence of methanol. It was seen that the hydrogen evolution rate was maximum for pristine NaTaO₃ samples, while it decreased for the La-Fe doped samples.

Figure 7.14 Photocatalytic hydrogen evolution from pristine, 2% La doped, and 2-6% Fe doped samples under UV-vis radiation (250-800 nm) (20 mL CH₃OH, 80 mL D.I. water).

Figure 7.15 Photocatalytic hydrogen evolution from pristine and La-Fe co-doped samples under UV-vis radiation (250-800 nm) (20 mL CH₃OH, 80 mL D.I. water).

To enable electron-hole separation, and explore the possibility of hydrogen evolution under visible radiation, platinum nanoparticles (0.05% co-catalyst), were deposited by the photodeposition method on both Fe doped and La-Fe co-doped samples. When Pt loaded samples were irradiated only with visible light ($\lambda > 390$ nm), the photocatalytic hydrogen evolution was obtained only from La-Fe co-doped samples. Fe doped samples did not show hydrogen evolution. Figure 7.15 shows the hydrogen evolution rates from 0.05% Pt loaded La-Fe co-doped samples. A maximum rate of $0.81 \mu\text{-moles}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ was obtained for 2% La-Fe co-doped sample. It was observed that the hydrogen yield dropped to lower values as the content of dopant increased.

Figure 7.16 Photocatalytic hydrogen evolution 0.05% Pt loaded La-Fe co-doped samples under visible radiation (20 mL CH₃OH, 80 mL D.I. water; $\lambda > 390$ nm).

The behavior of the visible light photocatalytic activity of Fe doped and La-Fe co-doped samples under visible irradiation can be explained on the basis of their crystals structures and band structures. Although Fe doped samples showed intense visible light absorption around 500 nm, they did not show any photocatalytic activity under visible radiation. The lack of photocatalytic activity could be attributed to the point defects produced on Fe doping as explained in the earlier section. Moreover, Fe ions may also act as electron traps thereby restricting the conduction of charge carriers [142]. It is known that Fe compounds lack carrier concentrations and due to which they exhibit poor photocatalytic activity [143, 144]. Earlier reports on have shown that higher concentration Fe doping is harmful for the photocatalytic activity [145-147]. On the other hand, in the case of La-Fe co-doping, the ionic charge balance could have led to minimum the point defects which are otherwise

produced on aliovalent doping. La-Fe co-doped samples also possessed peculiar surface morphology i.e. surface nanosteps. Kudo et al. showed that surface nanosteps are highly beneficial for the photocatalytic water splitting reactions as it separates the H₂ and O₂ reaction centers and prevents the back-reaction [21]. Therefore, due to possible advantages of the charge balance (reduced defects) and surface nanosteps, La-Fe co-doped samples showed photocatalytic hydrogen evolution under visible radiation. Further investigations are needed to understand and improve photocatalytic activity of Fe doped NaTaO₃ samples.

7.7 Summary

Visible light active powders of Fe and La-Fe co-doped NaTaO₃ were prepared by the conventional solid state route. The crystal structure, surface structure and optical properties of these powders were studied in detail. It was showed that co-doped NaTaO₃ powders were active under the visible light for the photocatalytic hydrogen evolution when loaded with Pt nanoparticles. Co-doping of La and Fe in equal amounts was found to be useful to generate characteristic nanosteps on the surface of NaTaO₃. It was revealed that the visible light response is caused by Fe doping at Ta sites while the surface nanosteps are produced by La doping in co-doped samples. For lower concentration of dopants i.e. 2% La and Fe each, the highest hydrogen evolution rate of 0.81 $\mu\text{moles}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ was obtained. Fe doped NaTaO₃ samples showed insignificant hydrogen evolution which was attributed to the point defects in the lattice.

Chapter VIII: Conclusions and Recommendations

This study systematically investigates doped NaTaO₃ systems for the potential visible light driven photocatalytic hydrogen generation. Using various experimental techniques, the crystal structure, optical properties, and photocatalytic performance of Bi doped NaTaO₃ and Fe, La-Fe co-doped NaTaO₃ powders have been studied in detail. The photocatalysts with optimum photophysical properties are subsequently developed. The main conclusions drawn from this study are stated below.

1. Based on the DFT calculations, we show that the doping of transition metals such as Mn, Fe, Cr, Cu, Ni and p block element Bi could be useful in reducing the band gap of NaTaO₃ and thus shift the absorption to the visible light region. The dopants such as Ti, Y, W, Sb, Ce, Sn, N, and In would not induce visible light response when doped alone. These results serve as a guide to the experimental work related to this phase in the future.
2. A novel photocatalyst, Bi³⁺ doped NaTaO₃ with unique dopant site occupancy and the band structure has been developed. The optimum synthesis conditions were found to narrow the band gap of Bi doped NaTaO₃ to as low as 2.64 eV. A correlation between synthesis conditions, crystal structure, and optical properties is established using experimental investigations as well as DFT studies. A good agreement between modeling and experimental results was observed. In this way, this study explains a complete synergy between crystal structure and optical properties which could be useful in further tuning of the photophysical properties. Bi doped NaTaO₃ powders showed MB degradation under the

visible radiation, and demonstrated a better performance than commercially available material P25. By loading appropriate co-catalyst (platinum) on the surface of Bi doped NaTaO₃, photocatalytic hydrogen generation rate of 0.86 $\mu\text{moles}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ was obtained under the visible light radiation. The present results indicate that Bi doping in NaTaO₃ could be a promising candidate for hydrogen evolution.

3. Nanoparticles of Bi doped NaTaO₃ could be prepared by low temperature hydrothermal route. These powders have an advantage of higher surface area; however they possess limited optical absorption in the visible region. Similar to the solid state samples, photocatalytic hydrogen evolution was observed under the visible light radiation after appropriate co-catalyst loading (7.5% Bismuth doping, 0.14% platinum loading, 0.72 $\mu\text{moles}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). The present results show that low temperature methods could also be a promising way to develop Bi doped NaTaO₃ photocatalysts.

5. Similar to bismuth doping, La-Fe co-doped NaTaO₃ powders have been developed as visible light active photocatalysts for the hydrogen evolution. Under the optimum conditions the photocatalyst showed a maximum hydrogen evolution rate of 0.81 $\mu\text{moles}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. In the case of La-Fe co-doped photocatalyst, we found that substituting La at Na site leads to the formation of characteristics nanosteps while substitution of Fe at Ta site induces visible light response in NaTaO₃.

6. This study opens a new venue to develop tantalate based photocatalysts. The experimental results show that doped NaTaO₃ systems are active of the visible light photocatalytic applications and doped NaTaO₃ can be promising candidates for the materials for solar

hydrogen. Although the doping of appropriate elements can achieve visible light absorption, our studies revealed that maintaining ionic charge balance in the lattice is critically important to achieve the visible light photocatalytic activity. In addition, the surface area of the samples also plays a key role in enhancing the photocatalytic hydrogen evolution generation.

Recommendations for the future work

1. The photocatalysts developed in this study show a potential for the visible light applications. However, efforts are needed to increase the efficiency of the photocatalytic activity in order to develop commercial applications. In the solid state route, the synthesis conditions of Bi doped NaTaO_3 powders can be further tuned to reduce the native point defects in the lattice. In hydrothermal synthesis the crystallinity of sample can be improved by post heat treatments. Improved crystallinity may enhance the photocatalytic properties of Bi doped samples. It also may help remove OH^- ions within the lattice.
2. It is known that loading of co-catalysts significantly enhances the photocatalytic activity. The loading of other types of co-catalysts such as NiO may improve the electron hole separation and contribute to increase the quantum yield. Literature on NaTaO_3 has shown that CB potentials of NiO and NaTaO_3 have similar energies which make the electron-hole separation efficient. Thus use of NiO as co-catalyst for Bi doped and La-Fe co-doped NaTaO_3 powders should be studied for the hydrogen evolution.

3. The present study shows that La-Fe co-doped NaTaO₃ is an active photocatalyst for hydrogen evolution under visible radiation. On account of its unique microstructure this compound can be further developed to enhance the yield of the hydrogen. Specifically, structural characterization of the samples could be done to study the distribution of the co-dopants in the lattice. The synthesis conditions can be tuned (multiple heat treatments, ball milling) to form the solid solution between LaFeO₃ and NaTaO₃. Further, increasing the carrier concentration in Fe-La doped system may benefit the photocatalytic activity.

4. In order to understand the optical properties of Fe and La-Fe co-doped systems, spin polarized band structure calculations should be carried out. DFT calculations of co-doped NaTaO₃ with different locations of co-dopants (distance between La and Fe) would shed light on possible optical absorption properties. This study shows that doping of certain elements can be useful in narrowing the band gap significantly. Additionally, computational studies on the co-doped NaTaO₃ such as W-N, W-Ce, La-Cr, La-Mn could be useful to identify visible light photocatalysts. Effort should be made to prepare co-doped NaTaO₃ photocatalyst where the doping itself compensates for the ionic charge imbalance.

List of Publications

Journal publications

1. **Pushkar D. Kanhere**, Jianwei Zheng, Zhong Chen, 'Site specific optical and photocatalytic properties of Bi doped NaTaO₃' *Journal Physical Chemistry C*, 2011, 115 (23), pp 11846–11853
2. **Pushkar Kanhere**, Jianwei Zheng, Zhong Chen, 'Synthesis, optical properties and photocatalytic hydrogen evolution over Bi³⁺ Doped NaTaO₃ photocatalyst, (*Article in Press to Intenational Journal of hydrogen energy*)
3. **Pushkar Kanhere**, Tang Yuxin, Gong Dang Guo, Jianwei Zheng, Zhong Chen, 'Hydrothermal synthesis and photocatalytic activities of Bi doped perovskite (NaTaO₃) and pyrochlore (Na₂Ta₂O₆) type sodium tantalate, (*To be submitted*)
4. **Pushkar Kanhere**, Jianwei Zheng, Zhong Chen, 'Electronic structure calculations of doped NaTaO₃ photocatalysts for visible light photocatalytic applications' (in preparation)
5. **Pushkar Kanhere**, Jianwei Zheng, Zhong Chen, 'Visible Light Active LaFeO₃-NaTaO₃ solid solution photocatalyst'. (*To be submitted*)

Conference Presentations

1. 'Optical properties of Bi doped NaTaO_3 ' 6th Asia and Oceania Photochemistry conference, Nov 2010, Wellington, New Zealand
2. 'Synthesis and visible light photocatalytic activities of Bismuth Doped NaTaO_3 Powders' International Conference on Materials for Advanced Technologies, (ICMAT) July 2011, Singapore

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Appendices

Appendix A

Table 1 Results of the Rietveld refinements of XRD patterns of Fe doped NaTaO₃

Fe doped NaTaO₃				
Sample	0%	2%	4%	6%
Cell Volume (Å ³)	236.082(54)	236.143 (84)	236.239 (12)	236.241 (12)
a (Å)	5.4863 (75)	5.4914(12)	5.4935 (16)	5.4935 (16)
b (Å)	5.5213 (71)	5.5187(10)	5.5211 (15)	5.5211 (14)
c (Å)	7.7936 (10)	7.7920(17)	7.7887 (25)	7.7887 (24)
Crystallite Size (nm)	180.0 (14)	172.4 (29)	166.6 (19)	167.5(19)
Strain (%)	0.1562 (20)	0.1988 (27)	0.1996 (38)	0.2011 (37)
Occupancy (Na)	--	0.000 (75)	0.0012 (56)	0.0077 (86)
Occupancy (Ta)	--	0.020 (75)	0.0388 (56)	0.0523 (86)
B _{Na} (Å ²)	1.205 (60)	1.43 (10)	1.291 (12)	1.29(11)
B _{Ta} (Å ²)	0.432 (95)	0.504 (16)	0.181(18)	0.157(17)
R _{wp} (%)	6.763	6.588	8.694	8.468
R _{Bragg} (%)	1.984	2.138	1.813	1.765