Synthesis and structural phase transformation study of co-doped V/Fe and V/Mn Titanium oxide: An experimental and DFT correlated study

M.Sc. Thesis

By HIMA M P



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Synthesis and structural phase transformation study of co-doped V/Fe and V/Mn Titanium oxide: An experimental and DFT correlated study

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> *by* **HIMA M P**



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2021



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Synthesis and structural phase transformation study of co-doped V/Fe and V/Mn Titanium oxide : An experimental and DFT correlated study** in the partial fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from JULY,2019 to JUNE,2021 under the supervision of Dr. Somaditya Sen, Assistant Professor, Department of Physics, Indian Institute of Technology, Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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Signature of PSPC Member #2 Date: 2021-06- 24

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DEDICATION

This thesis is dedicated to my parents for the unconditional love, support, and care.

Abstract

TiO₂ plays an essential role in both experimental and theoretical fields of research because of its intriguing electrical structures and broad band gap. Large-scale uses of TiO₂ are primarily based on its great efficiency in photocatalysis, pigmenting, solar cells, fuel cells, solar cells, various sensors, pollution control systems, waste management, and self-cleaning glass coating materials, as well as food, paint, cosmetics, UV protection, and other applications. It is used to produce hydrogen by splitting water and to cleanse contaminated air or water, therefore it is also ecologically friendly. Antifogging and self-cleaning coatings made of TiO₂ have been utilised on glass. It's also approved for use as a food and medicinal ingredient. TiO₂ have versatile application and it includes its application as a molecular sieve in oxy-concentrator. The demand of oxy-concentrator has increased due to current covid scenario as the death rate is increased due to unavailability of oxygen cylinders. TiO₂ adsorbents have a higher working capacity and selectivity for air separation by preferentially adsorbing nitrogen from air for oxygen production.

A theoretically supported experimental study of the TVFO and TVMO solid solution is being reported for the first time. Correlation of structural change was extensively investigated using x-ray diffraction (XRD) measurements, Raman and density functional theory (DFT) calculation. A detailed study of the structural lattice parameters, bond lengths, bond angles, vibrational and electronic properties have been emphasized. All the above parameters show a strong correlation with the structural change. The vibrational properties were studied experimentally and supported by DFT phonon calculations, specifying the displacement pattern (eigen vectors) corresponding to each mode which provides deeper insight into the lattice dynamics of the compounds. The optoelectronic modifications in the band properties were studied experimentally and theoretically. Considerable band gap tuning of UV to visible range was observed for TVMO samples which is important from the prospective of application. Hence, this manuscript is an in-depth analysis of the structurecorrelated study of the TVFO and TVMO solid solution.

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Chapter 1

INTRODUCTION

This chapter introduces all the basic concepts required to effectively appreciate the research work presented in this thesis. It begins with an introduction to the material used in this study, Titanium dioxide (TiO₂), and its importance. Three phases of TiO₂ are discussed in detail. Also, a brief explanation of space group is provided here. The last portion gives information about the phase transition in the material, i.e. what are the factors affecting phase transition.

1.1 Titanium dioxide and its importance

Titanium is the tenth most abundant element on the planet. Plants and animals are the most prevalent hosts. Titanium oxides are formed when titanium reacts with oxygen in nature and may be found in ores, indigenous dusts, sands, and soils. Pure titanium oxide is a fine white powder that may be used to make a brilliant white pigment[1]. TiO_2 is a non-toxic, inert substance that has been utilised in a variety of applications for decades. In the presence of light with an energy equivalent to or higher than its band gap energy, it is a semiconducting material that also shows photocatalytic activity. Titania has received a lot of attention over the years because of the comparatively inexpensive cost of the raw material and its processing. Because of its intriguing electrical structures and broad band gap, TiO_2 plays an essential role in both experimental and theoretical fields of research. Several procedures may be used to tune the band gap. The importance of TiO_2 is demonstrated by the fact that it is produced in large quantities all over the world.

 TiO_2 is used in a variety of technical and industrial settings. Large-scale uses of TiO_2 are primarily based on its great efficiency in photocatalysis, pigmenting, solar cells, and UV absorption, among many other uses. Research is being conducted with the goal of improving the functions of all forms of TiO_2 , including single crystal, nanoparticles, thin films, and bulk. TiO_2 is used in fuel cells, solar cells, various sensors, pollution control systems, waste management, and self-cleaning glass coating materials, as well as food, paint, cosmetics, UV protection, and other applications. It is used to produce hydrogen by splitting water and to cleanse contaminated air or water. Non-toxicity, chemical stability, limited solubility, and a high refractive index are some of the features that make it useful for industrial purpose. Antifogging and self-cleaning coatings made of TiO_2 have been utilised on glass. It's also approved for use as a food and medicinal ingredient.

Due to current covid scenario when death rate is increasing due to unavailability of oxygen cylinders, the demand of oxy-concentrator has increased. Oxy-concentrator is used for the selective adsorption of nitrogen in air for oxygen production. TiO_2 have versatile application and it includes its application as a molecular sieve in oxy-concentrator. TiO_2 adsorbents have a higher working capacity and selectivity for air separation by preferentially adsorbing nitrogen from feed air for oxygen production. As a result, the amount of adsorbent and power required to produce oxygen under similar process conditions are much lower compared to other adsorbents. Therefore, the synthesized TiO_2 is currently the best adsorbent for oxygen production from air [2].

1.2 Phases of TiO₂

The fundamental hypothesis suggested by Professor W. L. Bragg reveals that if a crystal is composed of large ions and small ions, its structure will approximate a close packed arrangement of the large ions (generally oxygen) alone. [3]. The small ions tucked in the interstices. The basis of the anatase and rutile structures, an octahedron with a titanium atom at its center and an oxygen atom at each corner. The rutile and anatase structures are both made of such octahedra sharing edges and corners with each other. In rutile and anatase, two edges and four edges respectively of each octahedron are shared. Both rutile and anatase are deformed in such a way as to cause each shared edge to be shortened as compared to regular octahedra, other edges being correspondingly lengthened.



Figure 1.1 Distorted octahedra occurring in rutile and anatase phase.

The distorted octahedra occurring in rutile and in anatase are shown in figure. Distortion is due the coulomb repulsion of the two quadrivalent metal ions brought near each other when an edge is shared will cause the titanium-titanium distance to increase until the repulsion of the two

oxygen ions defining. Both anatase and rutile is a coordination structure, with six oxygen atoms about each titanium atom and three titanium atoms about each oxygen. As a result of these considerations the following assumptions were made: In rutile, there occur strings of octahedra in parallel orientation connected by shared edges; these strings, which extend in the direction of the c-axis, then are connected by sharing corners to form the complete crystal. The staggered strings are represented in Fig. 3- Brookite unit of structure contains four octahedra ($4 TiO_2$), The basic distorted octahedron is shown in Fig. 6. The suggested structure places eight titanium atoms and two groups of eight oxygen atoms each in the positions 8c.



Figure 1.2 Octahedral structure of TiO_2 . the central atom corresponds to titanium and six atoms surrounding it are oxygen atoms. Octahedral molecular geometry describes the shape of compounds with six atoms or groups of atoms symmetrically arranged around a central atom, defining the vertices of an octahedron. The octahedron has eight faces, hence the prefix octa. The different arrangement of these TiO6 Octahedra gives rise to different phases.

TiO₂ mainly has three naturally occurring polymorphs. In order of abundance, these are rutile (tetragonal, space group- $P4_2/mnm$), anatase (tetragonal, space group- $I4_1/amd$), and brookite (orthorhombic, space group-Pbca) [4]. Anatase and brookite are of metastable phase, whereas rutile is the stable phase. Brookite is rarely available and commercial synthesis of brookite is very difficult due to its extremely unstable structure. The structure of TiO₂ is made of different arrangements of TiO₆ octahedra and the phase changes when related orientation between neighbouring octahedra is altered. Anatase to Rutile phase transition is not a displacive one, but it is a reconstructive process where breaking and reforming of bonds take place. The difference between the three phases originates from the number of corners and edges shared by the octahedra. Anatase shares four edges and four corners, Brookite shares three edges and five

corners and Rutile shares two edges and six corners. Surface energy of anatase is very low when compared to that of rutile. So anatase can be formed at room temperature [5].



Figure 1.3 Structure of (a) anatase (b) rutile (c) brookite.

The space group of three phases of TiO₂ are different as Ti and O₂ site symmetry elements are different. For anatase phase, Ti-site (4a) symmetry elements is -4m2 and O-site (8e) symmetry elements is 2mm where m is mirror plane, 4 is four fold rotation and 2 is two fold rotation. For rutile phase, Ti-site (2a) symmetry elements is mmm and O-site (4f) symmetry elements is m2m where m is mirror plane and 2 is two fold rotation. For brookite phase, Ti-sites (8c) and O-site (8c) symmetry elements is 2mm where m is mirror plane, 4 is four fold rotation and 2 is two fold rotation. The space group of Anatase is $I4_1/amd$. I denotes body centred bravais lattice, 41 denotes 4 fold rotation with 1/4 translation (screw axes), / denotes plane perpendicular to principle axis (symmetry axis), a denotes glide plane with translation x+1/2 [x, y, z $\rightarrow x+1/2$, y, \overline{z}], m denotes mirror plane and d denotes the glide plane with translation x+1/4, y+1/4 [x, y, z \rightarrow x+1/4, y+1/4, \overline{z}]. The space group of Rutile is *P4₂/mnm*. P denotes Primitive bravais lattice, 4₂ denotes 4-fold rotation with $\frac{1}{2}$ translation (screw axes), / denotes the plane perpendicular to principle axis (symmetry axis), m denotes mirror plane, n represents glide plane with translation x+1/2, y+1/2 [x, y, z $\rightarrow x+1/2$, y+1/2, \overline{z}]. The space group of brookite is Pbca [6]. Due to different space group, number of Raman actives phonon modes varies for three phases of TiO₂. Raman active modes for Anatase, Rutile and Brookite are six, four and twelve respectively [53]. Due to different point group symmetry (atomic sites) present in different space group leads to different character table for these three phases, Anatase, Rutile and Brookite [table].

se

Character Table¹

D _{4h} (4/mmm)	#	1	2	4	2100	2 ₁₋₁₀	-1	mz	-4	m ₁₀₀	m ₁₋₁₀	functions
Mult.	-	1	1	2	2	2	1	1	2	2	2	÷
A _{1g}	Γ ₁ +	1	1	1	1	1	1	1	1	1	1	x ² +y ² ,z ²
A _{2g}	Γ ₂ +	1	1	1	-1	-1	1	1	1	-1	-1	Jz
B _{1g}	Γ ₃ +	1	1	-1	1	-1	1	1	-1	1	-1	x ² -y ²
B _{2g}	۲ ₄ +	1	1	-1	-1	1	1	1	-1	-1	1	ху
Eg	Г ₅ +	2	-2	0	0	0	2	-2	0	0	0	$(xz,yz),(J_X,J_y)$
A _{1u}	Г ₁ -	1	1	1	1	1	-1	-1	-1	-1	-1	
A _{2u}	Г2 ⁻	1	1	1	-1	-1	-1	-1	-1	1	1	z
B _{1u}	Г ₃ -	1	1	-1	1	-1	-1	-1	1	-1	1	
B _{2u}	Г4 ⁻	1	1	-1	-1	1	-1	-1	1	1	- <mark>1</mark>	
Eu	Г ₅ -	2	-2	0	0	0	-2	2	0	0	0	(x,y)

Table 1.1.b Character table of Rutile

Character Table¹

D _{4h} (4/mmm)	#	1	2	4	2 ₁₀₀	21-10	-1	mz	-4	m ₁₀₀	m ₁₋₁₀	functions
Mult.	-	1	1	2	2	2	1	1	2	2	2	100
A _{1g}	۲ ₁ +	1	1	1	1	1	1	1	1	1	1	x ² +y ² ,z ²
A _{2g}	Γ ₂ +	1	1	1	-1	-1	1	1	1	-1	-1	Jz
B _{1g}	Г ₃ +	1	1	-1	1	-1	1	1	-1	1	-1	x ² -y ²
B _{2g}	Γ ₄ +	1	1	-1	-1	1	1	1	-1	-1	1	ху
Eg	Γ ₅ +	2	-2	0	0	0	2	-2	0	0	0	$(xz,yz),(J_X,J_y)$
A _{1u}	Г ₁ -	1	1	1	1	1	-1	-1	-1	-1	-1	-
A _{2u}	Г2 ⁻	1	1	1	-1	-1	-1	-1	-1	1	1	z
B _{1u}	Г3 ⁻	1	1	-1	1	-1	-1	-1	1	-1	1	
B _{2u}	Г4 ⁻	1	1	-1	-1	1	-1	-1	1	1	-1	-
Eu	Г ₅ -	2	-2	0	0	0	-2	2	0	0	0	(x,y)

Table 1.1.c Character table of Broo	kite
-------------------------------------	------

Character Table¹

D _{2h} (mmm)	#	1	2 _z	2 _y	2 _x	-1	mz	my	m _x	functions
Ag	Γ ₁ +	1	1	1	1	1	1	1	1	x^{2},y^{2},z^{2}
B _{1g}	<mark>Г</mark> 3 ⁺	1	1	-1	-1	1	1	-1	-1	xy,J _z
B _{2g}	Γ ₂ +	1	-1	1	-1	1	-1	1	-1	xz,J _y
B _{3g}	Г ₄ +	1	-1	-1	1	1	-1	-1	1	yz,J _x
A _u	Г <mark>1</mark> Т	1	1	1	1	-1	-1	-1	-1	•
B _{1u}	Г ₃ -	1	1	-1	-1	-1	-1	1	1	Z
B _{2u}	Г ₂ -	1	-1	1	-1	-1	1	-1	1	У
B _{3u}	Г <mark>4</mark> ⁻	1	-1	-1	1	-1	1	1	-1	x

Symmetry operation is a mathematical operation that leads to a self consistent or indistinguishable lattice point. They are point group and space group symmetry operation. Any symmetry operation performed about a point or a line are called point group and if this point group symmetry elements (translation, rotation, reflection, inversion, rotatory inversion) are translated with space constitutes the space group. Space group are of two types, screw axes and the glide plane. If translation and rotation is performed simultaneously, then it is called screw axes. If translation and reflection is performed simultaneously, then it is called glide plane. Different physical and chemical characteristics of TiO2, such as density, bandgap, refractive index, hardness, dielectric permittivity, and so on, vary depending on crystal structure. [7][8]These rules regulate its multipurpose uses and usage.

1.3 Phase Transition

A material's physical and chemical characteristics are heavily influenced by its crystal structure. As a result, the application of any material is heavily reliant on qualities that are governed by the crystal structure.

Among the three polymorphs, anatase and brookite are metastable phases while rutile is the most thermodynamically stable phase [9]. The arrangement of the fundamental TiO_6 octahedra

building pieces produces varied characteristics in all three phases [8]. The difference between the three phases stems from the Ti-O bond length in TiO₆ octahedra and the number of common corners and edges among the octahedra, as described previously. At lower temperatures, the anatase crystalline phase of TiO₂ is easily produced. This is because anatase has a lower surface free energy than rutile, despite the fact that rutile has a smaller Gibbs free energy [9]. Brookite is an uncommon mineral [10][9]. The commercial production of brookite TiO2 is extremely challenging. It's only accessible as solitary natural crystals [11]. Metastability exists in both the anatase and brookite phases. A first order phase transition [11] occurs when both metastable phases are irreversibly and exothermally transformed to rutile phase as temperature rises. According to accounts, however, it is uncertain whether this transition occurs in the order anatase-brookite-rutile or brookite-anatase-rutile. Ye et al. have proposed a brookite-anatase-rutile pathway. Mitsuhashi and Kleppa et al. [12] have proposed an anatase → brookite → rutile based on calorimetric measurements of phase transition enthalpies. Thermodynamic phase stability is analogous to anatase \rightarrow brookite \rightarrow rutile, according to them. This permits the anatase phase to either change straight to rutile phase or move through an intermediate brookite phase to rutile phase. The phase conversion of anatase \rightarrow rutile(A \rightarrow R) is not a straightforward distortive/displacive phase transformation. The breaking and reformation of bonds results in a thorough structural rebuilding. During the AR phase change, the a and b lattice constants increase while the c lattice constant contracts, resulting in an 8% reduction in unit cell volume [11][5]. The anatase and rutile phases of TiO2 are used in the majority of applications. As a result, it is critical to understand the variables that influence grain development and the delay/promotion of $A \rightarrow R$ phase change. The grain growth process and the delay/promotion of $A \rightarrow R$ phase transitions are influenced by a number of variables. The grain development and therefore transformation is controlled by synthesis processes, environment, pressure, calcination temperature/time, strain, starting crystallite size, presence of dopants, pH, defects and impurities, and so on.

Chapter 2

REVIEW OF PAST WORK

2.1 Introduction

Titanium dioxides (TiO₂) have been extensively researched due to their intriguing general properties in a variety of fields such as catalysis, photocatalysis, and antibacterial agents, as well as in civil applications such as nano-paint (self-cleaning) that have an impact on people's quality of life. Ruixiang Li et al. [10] observed that to enhance the effectiveness of environmental treatment, the synthesis and development of TiO2 has become a hot issue. In photocatalyst technology, TiO2 is the most extensively used catalyst, and it also plays an important role in removing pollutants from the soil. Kuang et al. [11] reported that after adding nano-TiO2, the Cd(II) removal efficiency of biological soil crusts rose by 27% compared to pure biological soil crusts.

The three polymorphs of TiO₂ are anatase, rutile and brookite. Brookite is converted to rutile by calcination at high temperatures. The transition takes place depending on a variety of parameters such as crystallite size, size distribution, and contact area of the crystallites in the powder. Zhang and Banfield [12]discovered a link between the three polymorphs' surface enthalpies and particle sizes. The energies of anatase, brookite, and rutile are so similar that tiny variations in surface energies can reverse them. For crystal diameters bigger than 11 nm, brookite is more stable than anatase, whereas rutile is the most stable phase for diameters bigger than 35 nm. Zhu et al. [13]developed an empirical equation for Dc, the crucial grain size of brookite that dominates the anatase-to-brookite transition sequence. When the size of brookite, Db is bigger than Dc, brookite converts straight to rutile, but when Db is smaller than Dc, brookite turns to anatase, which subsequently converts to rutile. The factors affecting phase transition includes synthesis processes, environment, pressure, calcination temperature/time, strain, starting crystallite size, presence of dopants, pH, defects and impurities, and so on.

The sol-gel method may readily produce pure rutile or mixed phases of anatase and rutile. According to Umadevi et al. [14], this method may produce anatase TiO_2 nanoparticles when heated at 500C for 5 hours. Temperature and time are critical factors in TiO_2 phase formation, crystal development, and phase transition. Buchholcz et al. [15] found that the sample is in anatase phase below 600 °C, and that when the temperature is increased (from 600 to 900 °C), the rutile phase appears. Apart from the calcination procedure, temperature, and duration, the

calcination atmosphere is an essential aspect that influences the relative phase stability of TiO₂ nanoparticles. According to Ahonen et al. [16]the $A \rightarrow R$ transition occurs at a greater temperature (580 °C) in a nitrogen environment than in an air environment (500 °C). On TiO₂ synthesis, decarburization, and denitrification, pressure has a substantial impact on phase formation, grain growth, and phase transition. Albetran et al. [17] investigated the influence of pressure on the transformation from the amorphous \rightarrow anatase \rightarrow rutile phase using in-situ synchrotron radiation x-ray diffraction. The solution's acidity/basicity (pH) is also a key component in controlling phase transition and grain development rate. The phase transition temperature falls as the pH of the sol-gel rises from 4.5 to 6.5. According to Tsega et al. [18] nanoparticles were produced by a sol-gel technique at varied pH values (3.2-6.8) and calcined at 500 °C for 2 hours. Strain is also a crucial factor in TiO₂ phase transition and grain development. Choudhury et al. [19]noticed a positive strain (0.0345) when particles are in the anatase phase and a negative strain (0.0006) when particles are in the rutile phase in their study. Moghaddam et al. [20]discovered a similar pattern of results. One of the most essential characteristics for anatase and brookite phase stability is crystallite size. It is also in charge of the A \rightarrow R phase change. According to several publications[21][22], the phase transition from anatase to rutile, as well as grain development rate, is influenced by the starting particle size of anatase TiO2. After 12 hours of age and heating at 250 °C, Sabyrov et al. [22] demonstrated that 3.1-3.7 nm sized crystallites change to 100 percent rutile of size 6-12.7 nm. Thus, as the original crystallite size shrank, the rate of phase change increased. Agglomeration and particle surface contact play a vital role in phase transition and grain development rate. Sabyrov et al. [22] found that densely agglomerated particles have a faster phase transition and a greater grain growth rate than loosely agglomerated particles.

2.2 Effects of dopants

With increase in temperature, both anatase and brookite phase got exothermally and irreversibly converted into Rutile phase. During anatase to rutile transformation, c-axis of anatase contracts, thus unit cell volume decreases. Hence the density of Rutile is more than that of Anatase. Anatase is an indirect bandgap semiconductor, Brookite is a direct bandgap semiconductor and Rutile has both direct and indirect bandgap which has almost similar values.

Reported research has shown that anatase can be formed at around 450C and anatase to rutile phase transition occurs between 450 C and 850 C temperatures[23].

Modifications can be done by introducing dopants in TiO_2 . Dopants such as Vanadium, chromium, gallium, copper, iron, manganese, cobalt, aluminium, nickel etc can be added to modify the properties of TiO_2 . Anatase to Rutile phase transition can be promoted or delayed by introducing dopants. For example, addition of elements like Lanthanum, Silicon, Niobium, Neodymium, Cerium, Strontium, Samarium etc. will delay the phase transition whereas the addition of elements like Vanadium, Iron, Manganese, Lithium, Cobalt, Sodium, Antimony etc. will promote the phase transition. And some elements even inhibit the phase transition, for example Gallium[5]. Dopant concentration not only affects the phase transition, it has a great impact on band gap energy too. Some elements like Vanadium, Nitrogen etc. decreases the bandgap energy[24] whereas some doped with TM where (TM= Fe0.1, Cr0.1, Fe0.06Cr0.04) increases the band gap energy of TiO₂[25].

Chapter 3

Experimental and theoretical methodology

The synthesis and characterization for $Ti_{(1-x)}V_{(x/2)}F_{(x/2)}O_2$ and $Ti_{(1-x)}V_{(x/2)}M_{(x/2)}O_2$ are briefly discussed in this chapter. A modified sol-gel process is used to synthesis the samples, which is then followed by successive high-temperature annealing. The following characterization techniques were used to investigate material properties: x-ray diffraction to confirm phase purity and crystal structure, Raman spectroscopy to study vibrational properties, and UV-Visible spectroscopy to calculate bandgap energy and urbach energy.

3.1 Sol-gel method:

This process is commonly used to make Ti and Si oxides. Precursors (of around 99.99 percent purity) are mixed in a specific proportion to achieve the necessary concentrations, which are then dissolved in dilute HNO3. Compounds containing the components necessary for sample preparation are known as precursors. Once that, gelling and burning agents are added to make a gel after they've been mixed. They produce a blackish powder when heated continuously at 80°C, and they are then annealed at a higher temperature (450°C) to remove carbon and nitrogen. As a result, samples with the required concentration are created.

3.1.1 Sample prepared by Sol-gel method:

The nanocrystalline powders of $Ti_{(1-x)}V_{(x/2)}F_{(x/2)}O_2$ and $Ti_{(1-x)}V_{(x/2)}M_{(x/2)}O_2$. $Ti_{(1-x)}V_{(x/2)}F_{(x/2)}O_2$ and $Ti_{(1-x)}V_{(x/2)}M_{(x/2)}O_2$ were synthesised (Pechini sol-gel process [54]) using high purity precursors of Ti (Dihydroxybis (AmmoniumLactate) Titanium (IV), 50 percent w/w aqueous solution), Fe (Iron (III)Nitrate Nona-hydrate, 98.0 percent), V₂O₅ and MnCO₃. By adding NH₄OH to deionized water, V₂O₅ dissolves and forms a pale yellowish solution [54]. Mn solution was made by dissolving MnCO₃ in water, adding few drops of dilute HNO₃ and stirring for half an hour. Fe solution was made by dissolving Fe(NO3)₃ in de-ionized water [54]. Following that, TALH is added dropwise to the V2O5 solution, along with Fe/Mn precursors, while the solution is swirled at room temperature, and the final solution is agitated for a further hour. In de-ionized water, a polymeric solution of citric acid (gelling agent) and glycerol (burning agent) was created. This solution was added to the precursor solution combination. This mixture is heated after another 30 minutes of stirring. The temperature is maintained at 80°C for 3–4 hours. A black gel is created, which is then burned in the air. Gels are generated by dehydration, and nano-powders are created by further burning in the ambience. The required phase was produced via de-carbonization and denitrification at 450C for 6 hours. Solid-state sintering was carried out at temperatures of 450°C ,500°C, 550°C, 600°C, 650°C, 700°C, 750°C, and 800°C.Thus $Ti_{(1-x)}V_{(x/2)}F_{(x/2)}O_2$ and $Ti_{(1-x)}V_{(x/2)}M_{(x/2)}O_2$ powder (*x*=0.00, 0.01, 0.03 and 0.06) is prepared by modified sol-gel synthesis. For all samples at all temperatures, processing factors such as environment, heating/cooling rates, and so on are kept constant.

For pure TiO2

 $C_{6}H_{18}N_{2}O_{8}Ti + C_{6}H_{8}O_{7} + (CH_{2}OH)_{2} \longrightarrow$ $(C_{2}H_{5}-O-Ti-O-C_{2}H_{5})_{n} \longrightarrow$ $\rightarrow TiO_{2} + H_{2}O\uparrow + N_{2}\uparrow + CO_{2}\uparrow$

For doped TiO2

 $C_{6}H_{18}N2O_{8}Ti + M+C_{6}H_{8}O_{7} + (CH_{2}OH)_{2} \longrightarrow$ $(C_{2}H_{5}-O-Ti-O-C_{2}H_{5}-O-M-O-C_{2}H_{5})_{n} \rightarrow Ti_{(1-x)}M_{x}O_{2} + H_{2}O\uparrow + N_{2}\uparrow + CO_{2}\uparrow$



Figure 3.1 Synthesising process of TVFO and TVMO

3.1.2 Computational Details

Spin-polarized DFT calculations were performed as implemented in the Quantum Espresso package (QE). The plane augmented wave (PAW) pseudopotentials [as in PSLLIBRARY 1.0.0] were used with the generalized gradient approximation based Perdew-Burke-Ernzerhof (PBE) functionals for the description of electron-ion interactions in TiO₂. A kinetic energy cutoff of 60 Ry was used for the representation of planewaves (wavefunctions) and a kinetic energy of 640 Ry was used for convergence of charge density and potential. A smearing width (σ) of 0.001 Ry was used for defining the electronic occupation with Methfessel-Paxton method. The convergence threshold of 10^{-10} Ry was set for the self-consistency. For the minimization of forces, the convergence criteria were set to 10^{-6} au. A finite-difference-based method was used for the calculation of phonon dispersion along the BZ as implemented in the PHONOPY package.

3.2 X-ray diffraction

3.2.1 Introduction:

An XRD is an experimental technique that uses the diffraction of X-rays in certain directions to identify the atomic or molecular structure of crystals all over the world. Cathode Ray Tubes (CRTs) create the X-rays, which are subsequently filtered to make them monochromatic, collimated to concentrate them, and aimed onto the samples[26]. The constructive interference of monochromatic X-rays at certain angles from each set of lattice planes of the sample produces XRD peaks. The lattice parameters, bond lengths, bond angles, and lattice deformation may all be determined by measuring the angles and observed intensity using diffraction data. The diffraction pattern is created using X-Rays, which have a wavelength of 0.1–100 nm.

3.2.2 Bragg's law:

When the incident X-rays interact with the sample, the sample creates constructive interference (and diffracted rays) if the following condition is met, which is known as Bragg's law. $2dsin \theta = n \lambda$

Where θ is diffraction angle, λ is the wavelength used in X-ray, d is the interplanar distance and n should be integral. In crystalline materials, this rule connects the X-ray wavelength to the diffraction angle and lattice spacing.

3.2.3 Working procedure:

The X-ray tube, sample holder, and detector are the three basic components of an X-ray diffractometer. They serve a special purpose in obtaining diffraction peaks. As previously stated, X-rays are created by burning the filament within a CRT to produce electrons, which are then accelerated by applying an accelerating potential to the target and then bombard the target. A distinct X-ray spectrum is formed when electrons have enough energy to remove electrons from the material's inner shells. These spectra consist of the most common K α and K β components. Now, K α contains two elements K α 1 and K α 2 (K α 1 has slightly less wavelength and twice the intensity of K α 2). The wavelengths are properties of the target materials (e.g., Cu, Fe etc.). To generate a monochromatic X-ray, these photons are further filtered out using foils or crystal monochromators. Because the wavelengths of K1 and K2 are so near, the average of their wavelengths is taken into account. Copper is the most typical target material for diffraction with Cu K α radiation (λ =1.5418Å). These X-rays are also collimated and directed toward the sample.



Figure 3.2 Schematic representation of X-Ray diffractometer

3.2.4 Miller Indices:

A Miller index is a technique of describing distinct crystal lattice planes in a unique fashion. The points that connect the a, b, and c axes should be located to establish the miller indices. The intercepts should then be calculated in a simplified fraction. The miller indices are obtained by taking the reciprocal of the fractions. They are commonly reffered to as (hkl) values.

3.2.5 Structural analysis:

Powder diffraction was formerly thought to be of little utility in crystallography due to the apparent superposition of intensities, which restricted the structural information. As a result, XRD was solely employed to determine the phase. However, throughout time, a process known as Rietveld refinement emerged, which extracts the most information from the crystal structure by fitting the curve of the complete XRD diffraction data. The use of XRD for structural analysis was revolutionised by this technology. Initially, this approach was created for neutron powder diffraction data, and afterwards for X-ray powder diffraction data. This refining approach is a curve fitting approach that takes multiparameters into consideration (taking into account multiple parameters). The improved data's output file contains information regarding crystal structure (lattice parameters, atomic positions, displacement factors etc.). In addition, data such as crystallite size, intrinsic strain, and crystallite; the phase fraction may be determined, which is explored in depth in the next chapter. For Rietveld refinement and profile matching, the GSAS 2 software is commonly used.

3.2.6 Rietveld- refinement:

In the Rietveld method, a model is fitted for a data. On being a correct model, it predicts what the 'true' values of intensities should be. The simulated values of intensity obtained from the model are labeled as $y_{c,i}$ where c stands for 'computed'. The Rietveld method optimizes the function of the model to minimize the weighted sum of the squared differences of the observed and computed intensities, i.e., it minimizes $\sum_i w_i (y_{c,i}-y_{o,i})^2$ where wi is labeled as weight and is equal to $1/\sigma^2[y_{o,i}]$ [27]. There is a straightforward index called weighted profile (R_{wp}), where Rwp2 = $\sum_i w_i (y_{c,i} - y_{o,i})^2 / \sum_i w_i (y_{o,i})^2$.

If there is an ideal model which gives the true value for each $y_{o,i}$, then there the average value of $(y_{c,i} - y_{o,i})^2$ becomes equal to $\sigma^2[y_{o,i}]$ and hence the expected value of $w_i(y_{c,i} - y_{o,i})^2$ becomes one. There is also a quantity "Rexp (the best possible Rwp)" called as expected R-factor (Rexp) can be expressed as Rexp=N/ $\Sigma_i w_i(y_{o,i})^2$ where N is the number of data points.

Again, a statistical term called "Chi squared (χ^2)" is introduced. Since the expected value of $(y_{c,i} - y_{o,i})^2 / \sigma^2[y_{o,i}]$ becomes one when the model is ideal. Therefore, the term χ^2 is defined as the average of these values. i.e. $\chi^2 = (1/N)\Sigma_i(y_{c,i} - y_{o,i})^2 / \sigma^2[y_{o,i}]$. This χ^2 value can also be determined by the ratio of $(Rwp)^2$ and $(Rexp)^2$ i.e. $\chi^2 = (Rwp)^2 / (Rexp)^2$. This χ^2 determines the goodness of fit of the curve.

At the time of the refinement process, χ^2 gets very large when the model is poor and thereafter, its value decreases as the model comes to a better agreement with data. The least-squares method in refinement never causes χ^2 to increase but the value may increase when the parameters are correlated. The value of χ^2 should never be less than one. The most appropriate way to get a quality Rietveld fit is by viewing the observed and calculated patterns graphically and it should also be ensured that the model is chemically plausible.

3.3 Optical and vibrational analysis:

Infrared and Raman spectra both show vibrational transitions. These are extremely sensitive tools that are used to study crystal lattice structure. When mercury discharge lamps were utilised as monochromatic sources and photographic film as detectors, the data acquired was considered a watershed moment. Photoelectric detectors were introduced in 1942, and lasers were employed as a source of excitation in Raman spectroscopy in 1966.

3.3.1 Raman Spectroscopy:

Raman spectroscopy is a non-destructive method for studying crystals and extracting information such as crystal structure, phase, crystallinity, and molecular interactions. A periodic pattern of atoms makes up the crystal lattice. Photons polarise the molecular electron cloud and leave it in a higher energy state when electromagnetic radiation is dispersed by sample molecules. This condition (a virtual state) is not stable, and photons are re-emitted as dispersed light in a relatively short amount of time.[28]. The majority of photons scatter back with their energy unaltered in this scattering event, i.e. the frequency of the scattered photons is equal to that of the input photons. Rayleigh scattering is the name for this sort of scattering. Only around 1 in 10⁷ photons are scattered back due to a change in their energy or frequency. Raman scattering is the term for this phenomenon.

When the molecule gains energy in the scattering process or photon loses its energy, the wavelength of the corresponding photon increases, which is known as Stokes Raman scattering (after G.G. Stokes). Conversely, when the molecule loses or photon gains energy, the wavelength of photon decreases and this is called Anti-Stokes Raman scattering.



Figure 3.3 Schematic diagram showing Raman scattering

Infrared (IR) spectroscopy, which is complementary to Raman spectroscopy, may also be used to investigate molecular vibrations. The only vibrations that may modify the polarisation vectors in IR spectroscopy are active, but the vibrations in Raman spectroscopy must modify the polarizability tensor. As a result, in centrosymmetric systems, a vibration cannot be both IR and Raman active, resulting in the complement of two vibrations. [29].



Figure 3.4 Schematic representation of Raman spectrometer

3.4 Optoelectronic study:

3.4.1 Absorption spectroscopy:

Different chemical species and substances have distinct colours, such as the green in cucumbers, the red in tomatoes, the green in chlorophyll, the yellow in quinone, the colorlessness in aspirin, and so on. All of these distinct hues are determined by light absorption in the visible area of the electromagnetic spectrum (EMW, 400-800 nm). When white light is irradiated on an object's surface, it may absorb one or more of the white light's components (here components refer to VIBGYOR). Those colours that aren't absorbed are reflected back to the observer. The tomato's shell, for example, reflects red light, whereas the cucumber's surface reflects green light. As a result, we may perceive many items of various hues in our daily lives. Light is a kind of electromagnetic wave (EMW) that travels at a very high speed. It's a mix of its several components, each of which has a particular wavelength or frequency. These elements combine to produce a spectrum known as the electromagnetic spectrum.

3.4.2 Lambert-Beer law:

UV Visible spectroscopy gives information about the absorption of radiation in the UV and visible regions of the electromagnetic spectrum. The molar absorptivity \mathscr{E} can be defined by Lambert-Beer law. According to this law, when light crosses a thin width of an absorbing sample, the intensity of light reduces and can be expressed in terms of transmittance (T).

 $T = I/I_0$

The absorbance of light for a sample is related to transmittance by following relations;

 $A = log_{10}(I/I_0)$

Further, the more light will be absorbed in a higher concentrated sample and the attenuation is also proportional to the width of the sample. On summarizing the above factors, absorbance can be given as

$$A = \mathscr{E}.c.l$$
,

where l is the width, c is concentration and \mathscr{E} is molar absorption coefficient (extinction coefficient) of the sample. The extinction coefficient is a sample-specific constant. This relation is known as Lambert-Beer law.

3.4.3 Tauc plot

The optical properties of $Ti_{(1-x)}V_{(x/2)}F_{(x/2)}O_2$ and $Ti_{(1-x)}V_{(x/2)}M_{(x/2)}O_2$ are observed using UV-Visible absorption spectra. The electronic band gap is estimated using Tauc equation[30]:

$$ahv = A(hv - E_g)^n$$
,

where, α is the absorption coefficient, A is a constant independent of the photon energy, hv is the incident photon energy, E_g is the electronic band gap, and n is a dimensionless parameter with n = 1/2 (direct allowed transitions) and n=2 (indirect-allowed transitions)[31][32]. For a direct band gap, Eg is calculated by plotting hv versus (α hv)² (with n =1/2). The extrapolation of the linear part of the graph on the (α hv)² axis gives the band gap[33][34].



Figure 3.5 Schematic representation of UV-Visible spectroscopy.



Figure 3.6 Schematic diagram of absorption spectrum

Chapter 4

Structural and optical properties of $T_{(1-x)}V_{(x/2)}Fe_{(x/2)}O_2$

In this chapter, the structural modification of TiO_2 by co-doping with vanadium and iron at Tisite has been extensively investigated using x-ray diffraction (XRD), Raman and UV-vis spectroscopy measurements and density functional theory (DFT) calculation followed by correlation study of structural, vibrational and electronic properties.

The vanadium doped TiO₂ has been reported by many researchers[35]. Tian et al. [36] have synthesized Vanadium-doped TiO₂ (X=0,0.02.04,0.08,0.12) powders by a sol-gel and studied the effect of annealing temperature (500 to 850 °C) on the magnetic properties. They have observed structure phase transform from anatase phase to rutile phase at annealing temperature 700 °C and an enhancement of room temperature ferromagnetism. From the XPS analysis, they have observed mixed valance state of vanadium i.e. Vi^{3+} and Vi^{5+} and for titanium Ti⁴⁺.Simeonov et al. [37] have studied Multi-layered anatase TiO₂ films doped with 0.03 and 1.2 at % vanadium, deposited on p-type Si substrates. They have reported that vanadium doping increases the conductivity of sol-gel anatase TiO₂ films and the specific resistivity was in the order of 10⁵ Ohm.cm. They have observed band gap of 3.3 eV for pure sample and 3.26 eV and 2.94 eV for 0.03 and 1.2 % doping respectively. Asgharinezhad et al. [38] have studied vanadium doped (x=0,1%) TiO₂ film annealed at 450C where XRD revealed single anatase phase. The decrement of band gap and resistivity from 3.71 to 3.65 eV and 16.7×10^7 to $1.7 \times$ 10⁷ ohm.cm respectively was observed by vanadium addition. Liu et al. [39] have enhanced the visible-light photocatalytic performance by Carbon-modified vanadium-doped TiO₂.Compared with vanadium doped TiO₂ sample and carbon modified TiO₂ sample, the 0.32C-0.5% V-TiO₂ photocatalyst exhibited excellent visible light activity. They have observed mixed valance state of vanadium (Vi^{3+} , Vi^{5+}) and titanium (Ti^{3+} , Ti^{4+}) and a decrease in band gap with doping. Chen et al. [40] have reported the photodegradation of sulforhodamine B on vanadium-doped TiO₂ montmorillonite (TiO₂-MMT) nanocomposites under visible light irradiation and a decrement of band gap from 3.06 to 2.14 eV in vanadium doped sample compare to pure TiO₂.

Similarly, many investigations have been reported on Iron doped TiO₂[]. Weng et al. [41] have prepared single anatase phase Fe doped TiO₂ thin films by spray pyrolysis deposition and observed that Fe doping can enhance water spreading on the thin film surface. XRD analysis showed single phase i.e. anatase for all the samples and UV–Vis spectra showed better hydrophilicity for Fe doped TiO₂ thin film which can attributed to the doped TiO₂ thin film with a narrower band gap. They have also reported that the role of Fe doping (x=0, 0.5, 1.0, 2.0, 5.0 %) can decrease the band gap from 3.36 to 3.13 eV and an increase in the ability of the films to absorb photon energy in visible spectrum. Hu et al. [42] have developed a green and sustainable photocatalytic semi-flexible pavement (SFP) for automobile exhaust (AE) purification using the iron (Fe)-doped titanium dioxide (TiO₂) loaded in the adsorbable hardened cement paste of SFP. The XRD analysis showed single phase i.e. anatase for all the prepared sample. the doping concentration 0.1%, 0.3% and 0.5% decreased the band gap starting from the pure TiO₂ 3.02 eV to 2.51, 2.34 and 2.32 eV respectively. AL-Jawad et al. [43] have also prepared Pure and Fe doped (3-6%) TiO₂ films by spin coating process annealed at 450 °C for antibacterial activity. XRD patterns confirmed the presence of anatase crystal structure showed for both pure and doped TiO2. From UV-vis spectrophotometry data, the results show an increment in the band gap by increasing the iron doping levels. The presence of the iron in titanium dioxide structure enhanced the antibacterial activity up to 97% and 100% against S. aureus and E. coli at 6% Fe-TiO₂ prepared films. Rajeswari et al. [44] have reported mixed phase (anatase and brookite) prepared by sol-gel method and from UV-visible spectroscopy data the optical bandgap of the 1%, 3% and 5% Fe doped TiO₂ thin films are found it around 3.63 eV, 3.41 eV and 3.11 eV respectively. But no combined study of vanadium and iron doped TiO₂ has yet been reported.

4.1 Synthesis

This standard Pechini sol-gel process was used to make nanocrystalline powders of $Ti_{(1-x)}V_{(x/2)}F_{(x/2)}O_2$ (*x*=0, 0.01, 0.03, 0.06, 0.09). TVFO were synthesised using high purity precursors of Ti (Dihydroxybis (AmmoniumLactate) Titanium (IV), 50 percent w/w aqueous solution), Fe (Iron (III) Nitrate Nona-hydrate, 98.0 percent) and V₂O₅. Details are given in chapter 2.

4.2 Structural studies

4.2.1 X-ray diffraction

X-ray diffraction (XRD) spectra was obtained from the Bruker D2-Phaser diffractometer. Xray source: Cu-anode (~1.5406 Å). The XRD confirms the phase purity and crystal structure of $Ti_{(1-x)}V_{(x/2)}Fe_{(x/2)}O_2$ (abbreviated as TVFO) at ambient temperature [Figure 4.1]. The TVFO samples annealed at 450 ° C shows mixed phase i.e. Anatase and Rutile. The XRD data reveals multiple peaks which can confirm the structural similarities of these samples to that of either tetragonal Anatase $I4_1/amd$ or Rutile $P4_2/mnm$ TVFO [Fig. 1(a)]. For TO (x=0) Anatase phase, thirteen prominent peaks were observed at 25.264°, 36.963°, 37.810°, 38.556°, 48.036°, 53.845°, 55.015°, 62.639°, 68.690°, 70.283°, 74.015°, 75.043°, 76.052°, and for Rutile phase, two small peaks were observed at 27.443°, 36.075°. For $0.01 \le x \le 0.09$, thirteen prominent peak were observed for Anatase phase whereas for Rutile phase the number of significant peaks varies with x. For x=0.01 and x=0.03, three prominent and one small peak were observed whereas for x=0.06 and x=0.09 seven peaks were observed. For x=0.06 four prominent and three small peaks and x=0.09 six prominent and one small peak. For $0.01 \le x \le 0.06$ the intensity gradually decreases and considerable decrement of intensity for x=0.09. Whereas in Rutile phase, the intensity gradually increases and considerable increment of intensity for x=0.09. The significant shifting of high intense peak (2θ =25.264 °) corresponding to Anatase phase is not observed with increase of x. However, for Rutile phase the high intense prominent peak $(2\theta=27.443^{\circ})$ shifts to lower angles for 0 < x < 0.03 and then to higher angles for x=0.06 and x=0.09. In the case of Rutile phase, interplanar spacing (d) increases for 0 < x < 0.03 and then decreases for x=0.06 and x=0.09. The interplanar spacing (d) first increases and further decreases due to the incorporation of equal Vanadium (V) and Iron (Fe) in the lattice. Hint, $Ti^{4+}(VI)$ (crystal radius 0.745Å), $Ti^{3+}(VI)$ (crystal radius 0.81Å) and $V^{3+}(VI)$ (crystal radius 0.78Å), $V^{4+}(VI)$ (crystal radius 0.72Å), $V^{5+}(VI)$ (crystal radius 0.68Å) and $Fe^{2+}(VI)$ (ls 0.75Å) and $Fe^{2+}(VI)$ (hs 0.92Å), $Fe^{3+}(VI)$ (ls 0.69Å) and $Fe^{3+}(VI)$ (hs 0.785Å). Note, the crystal radius of V^{4+} , V^{5+} , $Fe^{3+}(ls)$ is lesser than crystal radius Ti^{4+} and also $Fe^{3+}(hs) \sim Ti^{4+}$. Hence, the increasing interplanar spacing (d) is an indication of V^{4+}/V^{5+} replacing Ti⁴⁺ in the TiO₂ lattice. On the other hand, the incorporation of V^{5+} will be associated with more O_2 incorporation in the lattice, due to the extra charge of the V^{5+} ion.



Figure 4.1 Room temperature XRD plot of TVFO annealed at 450°C



Figure 4.2 Rietveld analysis of XRD pattern of TVFO annealed at 450 °C

Rietveld refinement (using GSAS software) for all the samples was performed to estimate their phase fractions and lattice parameters. Rietveld analysis established that all samples annealed at 450 ° show a mixed phase i.e. tetragonal Anatase ($I4_1/amd$) and Rutile ($P4_2/mnm$). The refined structural parameters (lattice parameters, atomic positions), along with the esd (estimated standard deviation), the thermal parameters and occupancies of various atomic sites, % phase fraction (% PF) have been shown in Table 4.1. The simulated data fits well with the experimental data for all samples, indicating the absence of impurity secondary phases [Figure 4.2]. Reasonably good fitting parameters, R_p and R_{wp} were obtained ~ <5% and <6%.

From the refinement, the density of the TVFO samples annealed at 450°C for Anatase phase was observed to increase from 3.893(x = 0) to 4.128 (x = 0.01) then decreases to 3.9 for x = 0.03 and further increases to 3.917 (x = 0.09). Hence, V and Fe co-doping, cell volume decreases as density increases with x. the density of the TVFO samples annealed at 450°C for Anatase phase was observed to increase from 3.893 (x = 0) to 4.128 (x = 0.01) then decreases to 3.9 for x=0.03 and further increases from 3.893 (x = 0) to 4.128 (x = 0.01) then decreases to 3.9 for x=0.03 and further increases to 3.917 (x = 0.09). Hence, V and Fe co-doping, cell volume decreases as density increases with x. Whereas, the density of the TVFO samples annealed at 450°C for Rutile phase was observed to increase from 4.25 (x = 0) to 4.506 (x = 0.01) then decreases to 4.261 for x = 0.03 and further increases to 4.276 (x = 0.09). Hence, V and Fe co-doping, cell volume decreases as density increases as density increases to 4.276 (x = 0.09). Hence, V and Fe co-doping, cell volume decreases as density increases as density increases to 4.261 for x = 0.03 and further increases to 4.276 (x = 0.09). Hence, V and Fe co-doping, cell volume decreases as density increases with x. TVFO 500 anatase-increases from 3.893 (x=0) to 4.129(x=0.01). TVFO 500 Rutile - increases from 4.25(x=0) to 4.508 (x=0.01) then decreases to 4.26 (x=0.03) then increase to 4.276 (x=0.09).

The TVFO samples annealed at 500° C also shows a mixed phase i.e. Anatase and Rutile. For TO (*x*=0) Anatase phase, thirteen prominent peaks were observed at 25.264°, 36.902°, 37.749°, 38.556°, 48.036°, 53.784°, 55.035°, 62.619°, 68.750°, 70.263°, 73.995°, 74.983°, 75.991°, and for Rutile phase, three prominent peaks were observed at 27.382°, 36.035°, 41.178° and one small peak at 55.035°. For *x*=0 and *x* = 0.01, mixed phase i.e. Anatase phase and Rutile phase and for $0.03 \le x \le 0.09$ a single Rutile phase is observed. For $0.03 \le x \le 0.09$ XRD pattern reveals eleven prominent peaks. The significant shifting of high intense peak (20=25.264°) corresponding to Anatase phase is not observed with increase of *x*. However, for Rutile phase the high intense prominent peak (20=27.382°) shifts to lower angles for $0 \le x \le 0.03$ and then to higher angles for *x*=0.06 and *x*=0.09. Similar shifting of peak in XRD spectra was observed for 500° C annealed samples. For $0 \le x \le 0.09$ the intensity of the peak corresponding to Anatase phase and corresponding to 500° C annealed at 450°C decreases as compared to 500°C annealed samples and increases incase of Rutile phase. In the case of Rutile phase, interplanar spacing (d) increases for $0 \le x \le 0.03$ and then decreases for *x*=0.06 and *x*=0.09 due to incorporation of V⁵⁺ ion and the possible reason is discussed in above section (TVFO 450 °C).

Rietveld refinement (using GSAS software) for all the samples was performed to estimate their phase fractions and lattice parameters. Rietveld analysis (Fig. 4.2) established that all samples annealed at 450°C show a mixed phase i.e. tetragonal Anatase ($I4_1/amd$) and Rutile ($P4_2/mnm$). Whereas for 500°C, mixed phase i.e. Anatase phase and Rutile phase for x=0 and x=0.01, and for $0.03 \le x \le 0.09$ a single Rutile phase is observed. The refined structural parameters (lattice parameters, atomic positions), along with the esd (estimated standard deviation), the thermal

parameters and occupancies of various atomic sites, % phase fraction (% PF) have been shown in Table 4.2

	% Phase fraction TVFO											
	450°C		500°C									
x	Anatase	Rutile	Anatase	Rutile								
0	98.94	1.06	98.94	1.06								
0.01	94.58	5.41	42.61	57.39								
0.03	96.35	3.64	-	100								
0.06	84.55	15.44	-	100								
0.09	50.23	49.76	-	100								

Table 4.1 Phase fraction of TVFO (450 °C and 500°C)

The simulated data fits well with the experimental data for all samples, indicating the absence of impurity secondary phases (Figure 4.4). Reasonably good fitting parameters, $R_p \sim <5\%$ and $R_{wp} < 6.52\%$ for 450 °C, 500°C were obtained. % Phase fraction obtained from Rietveld refinement of 450 °C XRD spectra reveals decrease of Anatase phase fraction from 98.94% for *x*=0 to 94.58% for *x*=0.01 and then increases to 96.35% (*x*=0.03) and further decreases to 50.23% (*x*=0.09). Whereas, for 500 °C % Anatase phase fractions decrease from 98.94% (*x*=0) to 42.61% (*x*=0.01) and % Rutile phase fraction increases from 1.06% (*x*=0) to 100% (*x*=0.09). V^{5+/3+}/ Fe³⁺ in place of Ti⁴⁺stabilize the structure and try to achieve most stable phase i.e. Rutile phase.



Figure 4.3 Room temperature XRD plot of TVFO annealed at 500 °C


Figure 4.4 Rietveld analysis of XRD pattern of TVFO annealed at 500 °C

From peak width, one can assess the (a) crystallite size [46] and (b) lattice strain [46]. The average crystallite size, D, is a measure of the size of a coherently diffracting domain and can be estimated using Scherrer's formula [47,48] (using EVA software): D= $k\lambda/\beta$ Cos θ , where, λ is the X-ray wavelength, β is the FWHM of the concerned peak, and θ is the diffraction angle. The average crystallite size of 450 °C anatase phase increases from ~21 nm (*x*=0) to ~61.47 nm (*x*=0.09) (Figure 4.5). Lattice strain ε , is a measure of crystal imperfections, such as lattice dislocation, non-uniform lattice distortions, etc. and can be estimated using the Williamson-Hall equation [46] given by $\varepsilon = \beta/(4 \tan \theta)$. With increasing *x*, the lattice strain first decreases from 7.9 (*x*=0) to 2.5 (*x*=0.09). (Figure 4.5). The average crystallite size of Rutile phase decreases from ~49.43 nm (*x*=0) to ~39.589 nm (*x*=0.06) then increases to 48.87 nm (*x*=0.09) (Figure 4.5). With increasing *x*, the lattice strain first increases from 0.0031 (*x*=0) to 0.0039 (*x*=0.06) then decreases to 0.0031 (*x*=0.09).

The average crystallite size of 500 °C anatase phase increases from ~27.03 nm (x=0) to ~ 34.47 nm (x=0.01) (Figure 4.5). Lattice strain ε increases from 0.061 (x=0) to 0.0048 (x=0.01). The average crystallite size of Rutile phase increases from ~46.98 nm (x=0) to ~ 62.42 nm (x=0.03) then decreases to 58.57 nm (x=0.06) and further increases to 61.73 nm (x=0.09). With increasing x, the lattice strain first decreases from 0.0033 (x=0) to 0.0025 (x=0.03) then increases to 0.0026 (x=0.06) and decreases to 0.0027 (x=0.06). V^{5+/3+}/ Fe³⁺ in place of Ti⁴⁺

invites more oxygen in the lattice which results reduction of strain and increase of crystallite size.



Figure 4.5 Crystalline size and lattice strain of TVFO, anatase and rutile phase, (450 $^{\circ}$ C and 500 $^{\circ}$ C).



Figure 4.6 Lattice parameter a,b,c of TVFO, anatase and rutile phase, (450 °C and 500 °c).

For 450 °C anatase phase, the lattice parameters (*a*, *b*) increase from 3.7845Å (*x*=0) to 3.7853 Å (*x*=0.01) then decreases to 3.7839 Å (*x*=0.06) and increases to 3.7843 Å (*x*=0.09) (Figure 4.6) Lattice parameter c increases from 9.5182Å (*x*=0) to 9.5188 Å (*x*=0.01) then decreases to 9.5108 Å (*x*=0.09). For the Rutile phase, the lattice parameters (*a*, *b*) increase from 4.5935Å (*x*=0) to 4.5949 Å (*x*=0.01) then decreases to 4.5932 Å (*x*=0.03) then increases to 4.5956 Å (*x*=0.06) and decreases to 4.5944 Å (*x*=0.09). Lattice parameter *c* decreases from 2.9589Å (*x*=0) to 2.9581 Å (*x*=0.03) then increases to 2.9595 Å (*x*=0.06) and decreases to 2.9579 Å (*x*=0.09). For 500 °C anatase phase, the lattice parameters (*a*, *b*) increase from 3.7845Å (*x*=0.01). For the Rutile parameter c increases from 9.5182 Å (*x*=0) to 9.5189 Å (*x*=0.01). Lattice parameter c increases from 9.5182 Å (*x*=0) to 9.5189 Å (*x*=0.01). Lattice parameters (*a*, *b*) increase from 4.5937 Å (*x*=0.01). For the Rutile phase, the lattice parameters (*a*, *b*) increase from 4.5937 Å (*x*=0.01) then decreases to 4.5934 Å (*x*=0.03) and continuously increases to 4.5946 Å (*x*=0.09). Lattice parameter c increases from 2.9589 Å (*x*=0.01) then decreases to 2.9578 Å. As crystallite size increases and lattice strain decreases with the corporation of V^{5+/3+}/ Fe³⁺.

Table 4.2 (a) Results from Rietveld refinement analysis for TVFO, anatase (450 °C). The esd's (estimated standard deviations) in the lattice parameters and atomic positions were obtained from GSAS software and is shown in the parenthesis.

			TVFO 450C AI	NATASE							
<i>x</i> (a)	Parame	ters									
0	a (Å) = 3.78449(6) b (Å) = 3.78449 (6) c (Å) = 9.51820(26)										
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy					
	Ti	0	0.25	0.875	0.00338	1.0					
	0	0	0.25	0.08263(14)	0.00471	1.0					
0.01	a (Å) =	3.78531(11) b (Å	a = 3.78531 (11) c (a)	Å) = 9.51878(51)							
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy					
	Ti	0	0.25	0.875	0.00314	0.99					
	0	0	0.25	0.08308(29)	0.00400	1.0					
	V	0	0.25	0.875	0.00690	0.05					
	Fe	0	0.25	0.875	0.8000	0.05					
0.03	a (Å) = 3.78524(10) b (Å) = = 3.78524(10) c (Å) = 9.51687(43)										
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy					
	Ti	0	0.25	0.875	0.00112	0.97					
	0	0	0.25	0.08272(24)	0.00801	1.0					
	V	0	0.25	0.875	0.025	0.015					
	Fe	0	0.25	0.875	0.025	0.015					
0.06	a (Å) =	3.78385 (12) b (Å	Å) == 3.78385(12) c	(Å) = 9.51538(32)	•						
	Ti	0	0.25	0.875	0.0027	0.94					
	0	0	0.25	0.08328(18)	0.00069	1.0					
	V	0	0.25	0.875	0.025	0.03					
	Fe	0	0.25	0.875	0.025	0.03					
0.09	a (Å) =	3.78429(10) b (Å	h = 3.78429(10) c (Å)	A) = 9.51084(43)							
	Ti	0	0.25	0.875	0.00679	0.910					
	0	0	0.25	0.08332(26)	0.00471	1.0					
	V	0	0.25	0.875	0.025	0.045					
	Fe	0	0.25	0.875	0.025	0.045					

Table 4.2 (b) Results from Rietveld refinement analysis for TVFO, rutile (450 $^{\circ}$ C). The esd's (estimated standard deviations) in the lattice parameters and atomic positions were obtained from GSAS software and is shown in the parenthesis.

			TVFO 4	450C RUTI	LE	
<i>x</i> (a)	Param	neters				
0	a (Å)	= 4.59370(0) b (Å	A = 4.59370(0) c	: (Å) = 2.95	870(0)	
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy
	Ti	0	0	0	0.00032	1.0
	0	0.305(8)	0.305(8)	0	0.00032	1.0
0.01	a (Å)	= 4.59493(72) b (Å) = 4.59493(72	c (Å) = 2.	95885(100)	
		x	У	z	$U_{iso}(\text{\AA}^2)$	Occupancy
	Ti	0	0	0	0.00593	0.99
	0	0.292(5)	0.292(5)	0	0.04781	1.0
	v	0	0	0	0.11057	0.05
	Fe	0	0	0	0.06473	0.05
0.03	a (Å)	= 4.59321(100) b	(Å) = 4.59321(1	00) c (Å) =	2.95811(141)	
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy
	Ti	0	0	0	0.00032	0.97
	0	0.304(6)	0.304(6)	0	0.04588	1.0
	v	0	0	0	0.02500	0.015
	Fe	0	0	0	0.02500	0.015
0.06	a (Å)	= 4.59559(75) b (Å) = 4.59559(75) c (Å) = 2.	95951(35)	
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy
	Ti	0	0	0	0.02437	0.94
	0	0.3056(10)	0.3056(10)	0	0.00180	1.0
	v	0	0	0	0.55754	0.03
	Fe	0	0	0	0.34497	0.03
0.09	a (Å)	= 4.59440(5) b (Å	A = 4.59440(5) c	(Å) = 2.95	788(6)	
		x	у	z	$U_{iso}(Å^2)$	Occupancy
	Ti	0	0	0	0.01977	0.91
	0	0.30511(34)	0.30511(34)	0	0.00144	1.0
	v	0	0	0	0.02500	0.045
	Fe	0	0	0	0.02500	0.045

Table 4.2 (c) Results from Rietveld refinement analysis for TVFO, anatase (500 °C). The esd's (estimated standard deviations) in the lattice parameters and atomic positions were obtained from GSAS software and is shown in the parenthesis.

	TVFO 500C ANATASE										
<i>x</i> (b)	Parameters										
0	a (Å) = 3.7	78170(5) b (Å)	= 3.78170 (5) c (Å) = 9.514	21(21)	_					
		x y z $U_{iso}(Å^2)$ Occupancy									
	Ti	0	0.25	0.875	0.00872	1.0					
	0	0	0.25	0.08357(14)	0.00010	1.0					
0.01	a (Å) = 3.7	78462(20) b (Å	= 3.78462(2)	20) c (Å) = 9.51	894(55)						
	Ti	0	0.25	0.875	0.00704	0.99					
	0	0	0.25	0.0804(4)	0.01266	1.0					
	V	V 0 0.25 0.875 0.025 0.05									
	Fe	0	0.25	0.875	0.025	0.05					

Table 4.2 (d) Results from Rietveld refinement analysis for TVFO, rutile (500 $^{\circ}$ C). The esd's (estimated standard deviations) in the lattice parameters and atomic positions were obtained from GSAS software and is shown in the parenthesis.

			TVF	O 500C RUTIL	E							
<i>x</i> (a)	Para	neters										
0	a (Å)	= 4.59222(45) b (Å) = 4.59222(45) c	(Å) = 2.95967(66)							
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy						
	Ti	0	0	0	0.00032	1.0						
	0	0.3125(26)	0.3125(26)	0	0.00032	1.0						
0.01	a (Å)	a (Å) = 4.59370(10) b (Å) = 4.59370(10) c (Å) = 2.95937(6)										
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy						
	Ti	0	0	0	0.03080	0.99						
	0	0.3056(4)	0.3056(4)	0	0.00032	1.0						
	v	0	0	0	0.02203	0.05						
	Fe	0	0	0	0.02506	0.05						
0.03	a (Å) = 4.59336(3) b (Å) = 4.59336(3) c (Å) = 2.95856(4)											
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy						
	Ti	0	0	0	0.01820	0.97						
	0	0.30512(34)	0.30512(34)	0	0.00421	1.0						
	v	0	0	0	0.02500	0.015						
	Fe	0	0	0	0.02500	0.015						
0.06	a (Å)	= 4.59417(4) b (Å	A) = 4.59417(4) c (Å	a) = 2.95856(4)	•							
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy						
	Ti	0	0	0	0.02887	0.94						
	0	0.30294(32)	0.30294(32)	0	0.01338	1.0						
	v	0	0	0	0.02500	0.03						
	Fe	0	0	0	0.02500	0.03						
0.09	a (Å)	= 4.59459(2) b (Å	A) = 4.59459(2) c (Å	a) = 2.95784(3)								
	Ti	0	0	0	0.03290	0.91						
	0	0.30809(25)	0.30809(25)	0	0.01624	1.0						
	v	0	0	0	0.02500	0.045						
	Fe	0	0	0	0.02500	0.045						

4.2.2 Raman spectroscopy:

From the above XRD analysis, it has been established that the co-doping (V/Mn) influences the structural parameters like bond length, tilting angle, crystal symmetry etc. These modifications are important enough to bring in changes in the vibrational properties of the constituent ions. To study these changes, Raman spectroscopy has been performed to explore how the phonon modes get modified due to chemical substitution (co-doping). The changes in atomic positions and chemical bond lengths commensurate with strain that are detected in the Raman spectrum through the changes in peak position or band broadening.

The Raman spectra were fitted using multiple peaks corresponding to known phonon modes. Lattice dynamics of the samples for pure TiO_2 (x = 0) was theoretically studied using Density Functional Theory (DFT). Eigenvectors (Vibrational pattern) of the phonon modes obtained from DFT calculations gave a better insight into the detailed lattice dynamics and the microscopic origin of each phonon mode. Experiment values of the phonon frequencies of TiO_2 were compared with simulated results from the DFT calculations.



Figure 4.7 Room temperature Raman spectra of TVFO, 450 °C

Bilbao Crystallographic Server is an <u>open access</u> website offering online crystallographic database and programs aimed at analysing and visualizing problems of structural crystallography. From Bilbao sever, one could get the information of how many Raman active modes are possible in a particular space group by selecting the correct atomic sites of atoms (Table 4.3).

WP	A _{1g}	A _{1u}	A _{2g}	A _{2u}	B _{1g}	B _{1u}	B _{2g}	B _{2u}	Eu	Eg
4a	•	•		•	1	·	•	•	•	1
8e	1	·	•	·	1	÷	•		•	2

Table: 4.3. Raman active modes of Anatase (space group No. 141: *I4*₁/*amd*, Ti (4*a*) and O(8*e*))

Table: 4.4. Raman active modes of Rutile (space group No. 136: P42/mnm, Ti (2a) and O(4f))

WP	A _{1g}	A _{1u}	A _{2g}	A _{2u}	B _{1g}	B _{1u}	B _{2g}	B _{2u}	Eu	Eg
2a	•	•	•	·	•	·	•	·	•	·
4f	1	•		2	1	Ŀ	1		•	1

Table: 4.5. Raman active modes of Brookite (space group No. 61: P42/mnm, Ti (8c) and O(8c))

WP	Ag	Au	B _{1g}	B _{1u}	B _{2g}	B _{2u}	B _{3g}	B _{3u}
8c	3	÷	3	·	3	•	3	·

These tables provide us the information that Anatase phase has total six Raman active modes at the Γ point (0, 0, 0). $A_{1g} + 2B_{1g} + 3E_g$. Here, *E* represents a doubly degenerate phonon mode, whereas *A* and *B* are nondegenerate phonon modes. A_{1g} is due to the oxygen vibration, one B_{1g} is due to Titanium and second B_{1g} is due to Oxygen vibration. For Rutile phase, total four Raman active modes i.e. $A_{1g} + B_{1g} + B_{2g} + E_g$ and these modes are due to only oxygen vibrations. For Brookite phase, total twelve Raman active modes i.e., $3A_{1g} + 3B_{1g} + 3B_{2g} + B_{3g}$ and these modes are due to both titanium and oxygen vibrations.

These modifications are important enough to bring in changes in the vibrational properties of the constituent ions. To study these changes, Raman spectroscopy has been performed to explore how the phonon modes get modified due to chemical substitution. The Raman spectra were fitted using multiple peaks corresponding to known phonon modes using FitYk software. Lattice dynamics of the samples due to Mn substitution was theoretically studied using Density

Functional Theory (DFT). Experiment values of the phonon frequencies were compared with simulated results from the DFT calculations.



Figure 4.8 DFT generated phonon modes of TiO₂, anatase phase, *I4₁/amd*



Figure 4.9 DFT generated phonon modes of TiO₂, rutile, *P4₂/mnm*



Figure 4.10 Correlation of Raman Shift with bond length obtained from XRD analysis for TVFO, anatase phase (450 °C)



Figure 4.11 Correlation of Raman Shift with bond length obtained from XRD analysis for TVFO, rutile phase (450 °C)

From DFT simulations, known modes are observed: E_g (1) (131.89 cm⁻¹), E_g (2) (166.08 cm⁻¹), B_{1g} (1) (375.73 cm⁻¹), B_{1g} (2) (476.43 cm⁻¹), A_{1g} (501.75 cm⁻¹), E_g (3) (620.50 cm⁻¹) for Anatase and B_{1g} (142.56 cm⁻¹), E_g (434.87 cm⁻¹), A_{1g} (577.09 cm⁻¹), B_{2g} (786.47 cm⁻¹) for Rutile.

For 450°C annealed samples, the Anatase $I4_1/amd E_g$ (1) (Figure 4.12) at ~ 143.549 cm⁻¹ is due to the vibrations of Ti and two O ions all vibrating along the same direction while third oxygen vibrate in opposite direction. The E_g (1) mode blueshifts from 143.549 cm⁻¹ (TO) to 145.825 cm⁻¹ (TVFO9). The Ti-Ti bond length is observed to decrease with substitution from 3.041 Å to 3.039 Å. The $I4_1/amd E_g$ (2) at ~ 197 cm⁻¹ is due to the vibrations of Ti in perpendicular direction and the two adjacent Ti vibrate in opposite direction. The E_g (2) mode blueshifts from

197 cm⁻¹ (TO) to 198.2 cm⁻¹ (TVFO1) then redshifts to 197.798 cm⁻¹ (TVFO6) and further blue shift to198.1 cm⁻¹ (TVFO9). The Ti-O bond length is observed to decrease with substitution from 1.935 Å (TO) to 1.934 Å (TVFO1) then increases to 1.935 Å (TVFO3) and further decrease to 1.9331 Å (TVFO6) then slightly increases to 1.9332 Å (TVFO9). The $I4_1/amd B_{1g}$ (1) at ~ 399 cm^{-1} is due to the vibrations of Ti in horizontal direction and the two adjacent Ti vibrate in opposite direction. The B_{1g} (1) mode redshifts from 399 cm⁻¹ (TO) to 395.120 cm⁻¹ (TVFO1) then blueshifts to 395.620 cm⁻¹ (TVFO3) further red shifts to 395.511 cm⁻¹ (TVFO6) followed by blueshift to 396.982 cm⁻¹ (TVFO9). The Ti-O bond length is observed to increase with substitution from 1.976 Å (TO) to 1.981 Å (TVFO1) then decrease to 1.977 Å (TVFO3) and further increase to 1.982 Å (TVFO6) then slightly decreases to 1.981 Å (TVFO9). The $I4_{1/amd} A_{1g}$ at ~ 513 cm⁻¹ is due to the vibrations of titanium and all three oxygen ions. Two Op ions vibrate opposite to Ti vibration and one oxygen in horizontal direction. The A_{1g} mode blueshifts from 513 cm⁻¹ (TO) to 517.275 cm⁻¹ (TVFO3) then redshifts to 516.182 cm⁻¹ (TVFO9). The Ti-O bond length is observed to decrease with substitution from 1.935 Å (TO) to 1.934 Å (TVFO1) then increases to 1.935 Å (TVFO3) and further decrease to 1.9331 Å (TVFO6) then slightly increases to 1.9332 Å (TVFO9). The $I4_1/amd E_g$ (3) at ~ 643 cm⁻¹ is due to the vibrations of one O_p and Ti in the horizontal and opposite direction, second O_p ions in the horizontal direction (parallel to Ti vibration) and Oa in horizontal direction. The E_g (3) mode redshifts from 643 cm⁻¹ (TO) to 639.72 cm⁻¹ (TVFO1) then blueshifts to 640.2 cm⁻¹ (TVFO3) and further redshift to 612.3 cm⁻¹ (TVFO9) followed by blueshifts to 638.81 cm⁻¹ (TVFO9). The Ti-O bond length is observed to increase with substitution from 1.976 Å (TO) to 1.981 Å (TVFO1) then decrease to 1.977 Å (TVFO3) and further increase to 1.982 Å (TVFO6) then slightly decreases to 1.981 Å (TVFO9).

For 450°C annealed samples, the Rutile $P4_2/mnm B_{1g}$ at ~ 144.857 cm⁻¹ is due to the vibrations of all O_p ions in horizontal along one direction. The B_{1g} mode blueshifts from 144.857 cm⁻¹ (TVFO1) to 146.731 cm⁻¹ (TVFO9). The Ti-O_a bond length is observed to decrease with substitution from 2.004 Å to 1.982 Å. The $P4_2/mnm E_g$ at ~ 447.9 cm⁻¹ is due to the vibrations of two Oa ions in horizontal and opposite direction. The E_g mode redshifts from 447.9 cm⁻¹ (TVFO1) to 443.168 cm⁻¹ (TVFO9) The Ti-O_P bond length is observed to increase with substitution from 1.897 Å (TVFO1) to 1.947 Å (TVFO9) The $P4_2/mnm A_{1g}$ at ~612.8 cm⁻¹ is due to the vibrations of two O_p ions towards each other and two O_a ions moves in vertically opposite direction. The B_{1g} mode redshifts from 612.8 cm⁻¹ (TVFO1) to 609.489 cm⁻¹ (TVFO9). The Ti-O_a bond length is observed to increase with substitution from 2.004 Å (TVFO1) to 1.982 Å (TVFO9).



Figure 4.12 Room temperature Raman spectra of TVFO, 500 °C



Figure 4.13 Correlation of Raman Shift with bond length obtained from XRD analysis for TVFO, anatase phase (500 °C)



Figure 4.14 Variation of Raman Shift with x for TVFO, rutile phase (500 °C)

For 500°C annealed samples, the Anatase $I4_{1}/amd E_{g}$ (1) mode blueshifts from 144.352 cm⁻¹ (TO) to 144.336 cm⁻¹ (TVFO1). The Ti-O_a bond length is observed to decrease with substitution from 1.984 Å (TO) to (TVFO1) 1.955 Å. The $I4_{1}/amd E_{g}$ (2) mode blueshifts from 197.071 cm⁻¹ (TO) to 197.233 cm⁻¹ (TVFO1). The Ti-O_a bond length is observed to decrease with substitution from 1.984 Å to 1.955 Å. The $I4_{1}/amd B_{1g}$ (1) mode redshifts from 395.936 cm⁻¹ (TO) to 395.172 cm⁻¹ (TVFO1). The Ti-O_a bond length is observed to decrease with substitution from 1.984 Å (TO) to 1.955 Å (TVFO1). The $I4_{1}/amd A_{1g}$ mode blueshifts from 517.701 cm⁻¹ (TO) to 517.779 cm⁻¹ (TVFO1). The Ti-O bond length is observed to decrease with substitution from 1.984 Å (TO) to 1.955 Å (TVFO1). The $I4_{1}/amd E_{g}$ (3) mode redshifts from 640.891 cm⁻¹ (TO) to 640.225 cm⁻¹ (TVFO1). The Ti-O_a bond length is observed to decrease with substitution from 1.984 Å (TO) to 1.955 Å (TVFO1). The Ti-O_a bond length is observed to decrease with substitution from 1.984 Å (TO) to 1.955 Å (TVFO1). The *I4*₁/amd *E*_g (3) mode redshifts from 640.891 cm⁻¹ (TO) to 640.225 cm⁻¹ (TVFO1). The Ti-O_a bond length is observed to decrease with substitution from 1.984 Å (TO) to 1.955 Å (TVFO1). The Ti-O_a bond length is observed to decrease with substitution from 1.984 Å (TO) to 1.955 Å (TVFO1). The *I4*₁/amd *E*_g (3) mode redshifts from 640.891 cm⁻¹ (TO) to 640.225 cm⁻¹ (TVFO1). The Ti-O_a bond length is observed to decrease with substitution from 1.984 Å (TO) to 1.955 Å (TVFO1). The Ti-O_a bond length is observed to decrease with substitution from 1.984 Å (TO) to 1.955 Å (TVFO1).

For 500°C annealed samples, the Rutile $P4_2/mnm B_{1g}$ mode redshifts from 141.223 cm⁻¹ (TVFO1) to 137.686 cm⁻¹ (TVFO9). As Rutile phase fraction for TO is less than 2% and hence Rutile peak is not observed. The $P4_2/mnm E_g$ mode redshifts from 450.012 cm⁻¹ (TVFO1) to 440.81 cm⁻¹ (TVFO9). The $P4_2/mnm A_{1g}$ mode redshifts from 613.721 cm⁻¹ (TVFO1) to 610.352 cm⁻¹ (TVFO9)

4.2.3 UV-vis spectroscopy

The optical properties of $Ti_{(1-x)}V_{(x/2)}F_{(x/2)}O_2$ are observed using UV-Visible absorption spectra. The electronic band gap is estimated using Tauc equation[30]:

$$\alpha h\nu = A(h\nu - E_g)^n$$
,

where, $\alpha \rightarrow$ absorption coefficient, A \rightarrow constant, hv \rightarrow incident photon energy, E_g \rightarrow band gap, and n = 1/2 (direct allowed transitions) and n = 2 (indirect-allowed transitions)[31][32]. Band structure (TiO₂) for both Anatase and Rutile obtained by DFT simulation reveals that the valence band maxima is majorly dominated by the O-states and conduction band minima dominated by the Ti-states. An indirect and direct bandgap is observed for Anatase and Rutile (Figure 4.15). The electronic transitions mainly occur between $\Gamma VB \rightarrow \Gamma CB$. DFT calculated bandgap value is closer to experimental value and other reports.

Bandgap plot (Figure 4.16) reveals that bandgap continuously decreases with V/Fe co-doping for both 450°C and 500°C annealed samples. Anatase and Rutile phase band gap was found to decrease from 2.89 eV to 1.512 eV and 3.105 eV to 2.49 eV respectively for TVFO 450°C

annealed samples. For TVFO 500°C annealed samples, Anatase and Rutile phase band gap was found to decrease from 2.914 eV (x = 0) to 1.855 eV (x = 0.01) and 3.204 eV to 2.089 eV respectively. The values of bandgap for TiO₂ for Anatase and Rutile phase are comparable to literature.

Hence, increase in the Ti-O bond strength for 450°C and 500°C annealed samples of Anatase phase highly reflect modifications of Eg. Interestingly, the Ti-O bond length decreases from 1.935 Å (x = 0) to 1.933 Å (x = 0.09) for 450°C and decreases from 1.935 Å (x = 0) to 1.933 Å (x = 0.09) for 450°C and 500°C respectively i.e., becomes stronger x. Similar trend is observed for the Raman mode Eg (1) which represents tilting. Strong hybridization/ overlapping of orbitals between Ti_{3d} and O_{2p} states can visualized by increase in \angle TiOTi with x .For Rutile phase (450°C), the Ti-O bond length overall shows decreasing trend from 1.95 Å (x = 0) to 1.947 Å (x = 0.09) for 450°C and 2.029 Å (x = 0) to 2.0019 Å (x = 0.09) for 450°C and 500°C respectively. Also, overall increase in \angle TiOTi with x are observed for both annealed samples.



Figure 4.15 UV-Vis spectra of TVFO for anatase and rutile phase (450°C and 500°C)



Figure 4.16 Variation of band gap and urbach energy with composition, x for TVFO, anatase and rutile phase ($450 \,^{\circ}$ C and $500 \,^{\circ}$ C)



Figure 4.17 DFT computed band structure of anatase



Figure 4.18 DFT computed band structure of rutile

However, it is noteworthy, that the width of defect bands, generally related to the strained electronic states are related to the Urbach tail states. The Urbach energy, E_u , can be expressed as a $\alpha = \alpha_0 \exp(h\nu/E_u)$ [79]; where, α_0 is a constant. Eu can be estimated by modifying the above relation as $\ln (\alpha) = \ln \alpha_0 + (h\nu/E_u)$. These states are extremely localized and characterize individual disordered states in a system. Interestingly, Eu continuously increases with V/Fe co-doping for both 450°C and 500°C annealed samples (Figure 4.16). Anatase and Rutile phase Eu was found to increase from 0.625 to 1.075 and 0.2 to 1.08 respectively for TVFO 450°C annealed samples. For TVFO 500°C annealed samples, Anatase and Rutile phase Eu was found to increase from 0.1654 to 0.2955 and 0.465 to 0.76717 respectively. With increasing *x*, the lattice strain decreases from 7.9 (*x*=0) to 2.5 (*x*=0.09).

Chapter 5

Structural and optical properties of T_(1-x)V_(x/2)Mn_(x/2)O₂

In this chapter, the structural modification of TiO_2 by co-doping with vanadium and manganese at Ti- site has been extensively studied using x-ray diffraction (XRD), Raman and UV-vis spectroscopy measurements and density functional theory (DFT) calculation followed by correlation study of structural, vibrational and electronic properties.

Many reports have been reported that Manganese doping has improved the photo-catalytic activity of TiO₂ for the decomposition of organic and inorganic compounds[45]. Sudrajat et al. [46] have observed the role, chemical identity, and local structure of the Mn dopants behind the improved photocatalytic activity of TiO₂. They have synthesised the sample by hydrothermal route method and annealed at 400°C temperature. XRD analysis showed single phase i.e. anatase TiO_2 with a tetragonal structure for $0 \le x \le 7.4$ and they have also observed shifts on the diffraction peaks to high angles on increasing the Mn concentration. This is because Mn cations partially replace Ti cations, forming a solid solution. Six Raman-active modes have also observed as it should for an anatase phase and doping with Mn also caused the E_{1g} band to shift to a high wavenumber that indicates lattice distortion, likely due to the partial replacement of Ti cations by Mn cations as mentioned earlier. The band gap energy was calculated to be 3.20, 3.18, 3.15, 3.10, and 3.02 eV for pure, 1.05%, 1.93%, 4.08% and 7.4 % doping with Mn respectively. Zhi et al. [47] have observed catalytic oxidation and capture of elemental mercury from simulated flue gas using Mn-doped titanium dioxide. They have synthesised the sample by solgel process with annealing temperature 500°C. The XRD analysis showed mixed phase i.e. anatase and rutile for pure TiO₂ and single anatase phase for X=1,3,5,10,15 mol% doping with manganese. The catalytic performance of the sample has increased by the addition of manganese in the TiO_2 due to partially conversion of Mn^{4+} to Mn^{3+} during the absorption process and the MnO_x was involved in the reaction with Hg^0 oxidation. Bharati et al. [48] have reported Structural Transformation and Photocatalytic Activity of Mn Doped TiO₂ Nanoparticles under Sunlight. They have synthesised the sample by solgel technique. The XRD analysis showed mixed phase i.e. anatase and rutile for doping concentration 1% and 2% and single anatase phase for 3% of Manganese in TiO2 six Ramanactive modes have also observed for the anatase phase but four Raman-active modes have observed for the rutile phase. Mn doped TiO₂ showed 80 to 100% photocatalytic degradation of dyes, such as rhodamine B and methylene blue and Congo Red under sunlight for an hour which is an important tool for the waste water treatment. Chauhan et al. [49] have reported Structural and photocatalytic studies of Mn doped TiO₂ nanoparticles. They have synthesized the sample by sol-gel method. The XRD analysis showed that the sample prepared at 100 C was largely amorphous that the samples calcined at 300 C and 800 C were composed of mainly anatase and partially rutile phase. They have also reported decrease in band gap from 3.00 eV to 2.95 eV with 3-10 mol % Mn doping at temperature 300 C. Mn-doped TiO2 exhibited excellent photocatalytic activity for the photodegradation of MB under visible light as compared to undoped TiO2 nanoparticles. Choudhury et al. [50] have reported Oxygen vacancy and dopant concentration dependent magnetic properties of Mn doped TiO₂ nanoparticle. They have synthesized the sample by sol-gel method. The XRD analysis showed single tetragonal anatase phase at low temperature and it converted to mixed i.e. anatase and rutile at higher temperature. They have also reported six Raman active modes and three infrared (IR) active modes for Anatase TiO₂. They have confirmed that Mn^{2+} ions undergo exchange interaction via oxygen vacancies and form bound magnetic polaron to induce ferromagnetism in TiO₂. At low doping concentration Mn^{2+} ions occupy lattice site, interact with oxygen vacancies and increases ferromagnetic ordering. However, at high dopant concentration some of the Mn²⁺ forms Mn₃O₄ phase and thereby increases paramagnetic contribution.

5.1 Synthesis

This standard Pechini sol-gel process was used to make nanocrystalline powders of $Ti_{(1-x)}V_{(x/2)}M_{(x/2)}O_2$ (*x*=0, 0.01, 0.03, 0.06, 0.09). TVMO were synthesised using high purity precursors of Ti (Dihydroxybis (Ammonium Lactate) Titanium (IV), 50 percent w/w aqueous solution), V₂O₅ and MnCO₃. Details are given in chapter 2.

5.2 Structural studies

5.2.1 X-ray diffraction

The powder X-ray diffraction (XRD) has been performed to confirm the phase purity and crystal structure of $Ti_{(1-x)}V_{(x/2)}Mn_{(x/2)}O_2$ (abbreviated as TVMO) at ambient temperature

(Figure 5.1). The TVMO samples annealed at 450 ° C shows mixed phase i.e. Anatase, Rutile and Brookite. The XRD data reveals multiple peaks which can confirm the structural similarities of these samples to that of either tetragonal Anatase $I4_1/amd$ or Rutile P4mm or Brookite *Pbca* TVMO. For $x \le 0.03$, mixed phase i.e. Anatase and Rutile and for x = 0.06 and x=0.09 Anatase, Rutile and Brookite phase were observed. For $0 \le x \le 0.09$ eleven prominent peak corresponding to Anatase were observed. For Rutile phase one weak peak is observed for x = 0. Eight peaks corresponding to Rutile phase were observed for $0.01 \le x \le 0.09$. For x = 0.06and x=0.09 one small peak corresponding to Brookite. The intensity of Anatase phase of 450° C samples remains constant for $0 \le x \le 0.09$, in addition to that no peak shift is observed for $0 \le x \le 0.09$. $x \le 0.06$ and a slight decrement of 20 is observed for x = 0.09. Whereas in Rutile phase, the intensity gradually increases and considerable increment of intensity for x = 0.09 and shifting of high intense Rutile peak ($2\theta = 27.4475^{\circ}$) towards lower 2θ values for $0 \le x \le 0.01$ then shift to higher 2θ value is observed with increase up to 0.09. While considering the Brookite phase the peak intensity increases and the shifting of peak is observed to higher 20 values for $0.06 \le$ x ≤ 0.09 . In the case of Rutile phase, interplanar spacing (d) for small doping (x = 0, 0.01) increases and for higher doping $(0.03 \le x \le 0.09)$ it continuously decreases. The interplanar spacing (d) first increases and further decreases due to the incorporation of equal Vanadium (V) and Iron (Fe) in the lattice. Hint, Ti⁴⁺(VI) (crystal radius 0.745Å), Ti³⁺(VI) (crystal radius 0.81Å) and $V^{3+}(VI)$ (crystal radius 0.78Å), $V^{4+}(VI)$ (crystal radius 0.72Å), $V^{5+}(VI)$ (crystal radius 0.68Å) and Mn²⁺(VI) (ls 0.81Å) and Mn²⁺(VI) (hs 0.97Å), Mn³⁺ (VI) (ls 0.72Å), $Mn^{3+}(VI)$ (hs 0.785Å), $Mn^{4+}(VI)$ (0.67Å). Note, the crystal radius of V^{4+} , V^{5+} , $Mn^{3+}(ls) Mn^{4+}$ is lesser than crystal radius Ti^{4+} and also $Mn^{3+}(hs) \sim Ti^{4+}$. Hence, the increasing interplanar spacing (d) is an indication of V^{4+}/V^{5+} replacing Ti⁴⁺ in the TiO₂ lattice. On the other hand, the incorporation of V⁵⁺ will be associated with more O₂ incorporation in the lattice, due to the extra charge of the V⁵⁺ ion. For x=0.06 and x=0.09, V³⁺ and Fe³⁺ possible charge state will not be able to introduce more oxygen and hence, the interplanar spacing (d) decreases for these (higher) doping. For x=0.06 and x=0.09, V^{3+} and Fe³⁺ possible charge state will not be able to introduce more oxygen and hence, the interplanar spacing (d) decreases for these (higher) doping. It is observed that higher doping (x = 0.06, 0.09) promotes Brookite phase in addition to Anatase and Rutile phase. Higher doping introduces more V⁵⁺in lattice as compared to lower doping. As result, the coulomb repulsion of the two quadrivalent metal ions with higher charge state (V5+) increases when brought near each other. Hence, an edge sharing will cause the titanium-titanium distance to increase until the repulsion of the two oxygen ions defining the shared edge becomes large enough to counteract the effect. This results in an orthorhombic Brookite phase.



Figure 5.1 Room temperature XRD plot of TVMO annealed at 450 °C



Figure 5.2 Rietveld analysis of XRD pattern of TVMO annealed at 450 °C



Figure 5.3 Room temperature XRD plot of TVMO annealed at 500 °C



Figure 5.4 Rietveld analysis of XRD pattern of TVMO annealed at 500 °C



Figure 5.5 Crystalline size and lattice strain of TVMO, anatase, rutile and brookite phase, (450 °C and 500 °C).



Figure 5.6 Lattice parameter a, b, c of TVMO, anatase, rutile and brookite phase, (450 °C and 500 °C).

Rietveld refinement (using GSAS software) for all the samples was performed to estimate their phase fractions and lattice parameters. Rietveld analysis (Figure 5.2) established that samples, $x \le 0.03$ annealed at 450 ° show a mixed phase i.e., tetragonal Anatase (*I4*₁/*amd*) and Rutile (*P4*₂/*mnm*). Whereas for samples, $0.03 \le x \le 0.09$ annealed at 450 ° show a mixed phase i.e. tetragonal Anatase (*I4*₁/*amd*), Rutile (*P4*₂/*mnm*) and Brookite *Pbca*. The refined structural parameters (lattice parameters, atomic positions), along with the esd (estimated standard deviation), the thermal parameters and occupancies of various atomic sites, % phase fraction (% PF) have been shown in Table 5.1 The simulated data fits well with the experimental data for all samples, indicating the absence of impurity secondary phases. Reasonably good fitting parameters, *R*_p and *R*_{wp} were obtained ~ <7.3% and <10.18%. From the refinement, the density

of the TVMO samples annealed at 450°C for Anatase phase was observed to increase from 3.893 (x = 0) to 4.129 (x = 0.01) then decreases to 3.902 for x = 0.03 and further increases to 3.935 (x = 0.09). Hence, V and Fe co-doping, cell volume decreases as density increases with x. Whereas, the density of the TVMO samples annealed at 450°C for Rutile phase was observed to increase from 4.25 (x = 0) to 4.511 (x = 0.01) then decreases to 4.275 for x = 0.03 and further increases to 4.296 (x = 0.09). Hence, V and Fe co-doping, cell volume decreases as density increases as density increases as density increases to 4.296 (x = 0.09). Hence, V and Fe co-doping, cell volume decreases as density increases to 4.296 (x = 0.09). Hence, V and Fe co-doping, cell volume decreases as density increases as density increases with x. The density of the TVMO samples annealed at 450°C for Brookite phase was observed to increase from 4.133 (x = 0.6) to 4.159(x=0.09).

The density of the TVMO samples annealed at 500°C for Anatase phase was observed to increase from 3.893 (x = 0) to 4.129 (x = 0.01) Hence, V and Fe co-doping, cell volume decreases as density increases with x. Whereas, the density of the TVMO samples annealed at 500°C for Rutile phase was observed to decrease from 4.25 (x = 0) to 3.025 (x = 0.01) then increases to 4.2688 for x = 0.03 and further decreases to 4.266 (x = 0.06) then increases to 4.286(x = 0.09). Hence, V and Mn co-doping, cell volume decreases as density increases with x. The density of the TVMO samples annealed at 450°C for Brookite phase was observed to increases from 4.142 (x = 0.06) to 4.15(x = 0.09).

The TVMO samples annealed at 500° C also shows a mixed phase i.e., Anatase and Rutile for $x \le 0.01$. For TO (x = 0) Anatase phase, eleven prominent peaks were observed at 25.26843°, 36.97085°, 37.75774°, 38.52445°, 48.00744°, 53.85865°, 55.02889°, 62.65564°, 68.70861°, 70.30256°, 75.06424° and for Rutile phase, two prominent peaks were observed at 27.38697°, 36.04273°. For x = 0 and x = 0.01, mixed phase i.e., Anatase phase and Rutile phase and for x = 0.03 only single rutile phase is observed. For $0.03 \le x \le 0.09$ XRD pattern reveals eleven prominent peaks. The significant shifting of high intense peak ($2\theta = 25.26843^{\circ}$) corresponding to Anatase phase is observed with increase of x and completely vanishes above x > 0.06. Also, for Rutile phase the high intense prominent peak ($2\theta=27.38697^{\circ}$) shifts to higher angles for 0 < x < 0.03 and then to lower angles for x = 0.06 and again shifted to higher angles for x = 0.09. The intensity of Anatase phase of 500° C samples decreases and peak shift to higher 20 values is observed for $0 \le x \le 0.01$. Whereas in Rutile phase, the intensity is very low for x = 0 and it increase for x = 0.01 then for $0.01 \le x \le 0.09$ intensity remains constant and also shifting of high intense Rutile peak ($2\theta = 27.3822$) towards higher 2θ values is observed for $0 \le x \le 0.03$ then a decrement to lower 20 value at x = 0.06 further shift to higher 20 values up to x = 0.09. While considering the Brookite phase the peak intensity increases and the shifting of peak is

observed to higher 20 values for $0.06 \le x \le 0.09$. In the case of Rutile phase, interplanar spacing (d) increases for $0 \le x \le 0.03$ and then decreases for x = 0.06 and x = 0.09.

Rietveld refinement (using GSAS software) for all the samples was performed to estimate their phase fractions and lattice parameters. Rietveld analysis (Fig. 4.5) established that all samples annealed at 450°C show a mixed phase i.e., tetragonal Anatase ($I4_1/amd$) and Rutile ($P4_2/mnm$). Whereas for 500°C, mixed phase i.e., Anatase phase and Rutile phase for x = 0 and x = 0.01, and for $0.03 \le x \le 0.09$ a single Rutile phase is observed. The refined structural parameters (lattice parameters, atomic positions), along with the esd (estimated standard deviation), the thermal parameters and occupancies of various atomic sites, % phase fraction (% PF) have been shown in Table 5.1. The simulated data fits well with the experimental data for all samples, indicating the absence of impurity secondary phases. Reasonably good fitting parameters, $R_p \sim <5\%$ and $R_{wp} < 6.52\%$ for 450 °C, 500°C were obtained. % Phase fraction obtained from Rietveld refinement of 450 °C XRD spectra reveals decrease of Anatase phase fraction from 98.94% for x = 0 to 39.24% for x = 0.06 and then increases to 71.836% (x = 0.09). Whereas, for 500 °C % Anatase phase fractions decrease from 98.94% (x = 0) to 42.61% (x =0.01) and % Rutile phase fraction increases from 1.06% (x = 0) to 100% (x = 0.09).

	% Phase	fraction	TVMO				
	450°C			500°C			
x	Anatase	Rutile	Brookite	Anatase	Rutile	Brookite	
0	98.94	1.06	-	98.944	1.0563	-	
0.01	91.37	86.31	-	25.992	74.008	-	
0.03	88.57	11.43	-	-	100	-	
0.06	39.24	23.13	37.63	-	99.912	0.088	
0.09	71.84	20.06	8.11	-	9.99	0.01	

Table 5.1 Phase fraction of TVMO (450 °C and 500°C)

From peak width, one can assess the (a) crystallite size and (b) lattice strain. The average crystallite size, D, is a measure of the size of a coherently diffracting domain and can be estimated using Scherrer's formula (using EVA software): $D = k\lambda/\beta Cos\theta$, where, λ is the X-ray wavelength, β is the FWHM of the concerned peak, and θ is the diffraction angle. Lattice strain ε , is a measure of crystal imperfections, such as lattice dislocation, non-uniform lattice distortions, etc. and can be estimated using the Williamson-Hall equation given by $\varepsilon = \beta/(4 \tan\theta)$. For TVMO 450⁰ C Anatase phase the average crystallite size increases from ~ 20.52 nm (x=0) to ~ 27.119 nm (x = 0.01) then decreases to 22.59 nm (x = 0.09) (Figure 5.5). With increasing x, the lattice strain first decreases from 0.0081 (x = 0) to 0.0061 (x = 0.01) then increases to 0.0073 (x = 0.09). In the case of Rutile phase, the average crystallite size increases from ~ 49.43nm (x=0) to ~ 51.83nm (x=0.03) then decreases to 47.26nm (x = 0.09), With increasing x, the lattice strain first decreases from 0.0031 (x=0.03) then increases 0.0032 (x = 0.09). For the Brookite phase average crystallite size decreases from ~ 42.67 nm (x = 0.06) to ~ 39.38 nm (x = 0.09), the lattice strain increases from 0.003 (x = 0.06) to 0.003 (x = 0.09) as x increases.

For TVMO 500C annealed samples having Anatase phase, the average crystallite size increases from ~ 27.03nm (x = 0) to ~ 37.18nm (x = 0.01), With increasing x, the lattice strain decreases from 0.0061 (x = 0) to 0.0044 (x = 0.01). Rutile phase shows increase in crystallite size from ~ 46.98nm (x = 0) to ~ 62.89 nm (x = 0.03) then decreases to 58.989nm (x = 0.09), while with increasing x, the lattice strain first decreases from 0.0033 (x = 0) to 0.0024 (x = 0.03) then increases to 0.0026 (x = 0.09). Brookite the average crystallite size decreases from ~ 51.26nm (x = 0.06) to ~ 49.79 nm (x = 0.09) With increasing x, the lattice strain increases from 0.0025 (x = 0.06) to 0.0026 (x = 0.09). V^{5+/3+}/ Mn³⁺ in place of Ti⁴⁺ invites more oxygen in the lattice which results reduction of strain and increase of crystallite size.

For 450 °C anatase phase, the lattice parameters (*a*, *b*) decrease from 3.784487Å (*x*=0) to 3.78422Å (*x* = 0.01) then increases to 3.78558Å (*x* = 0.06) and decreases to 3.77957 Å (*x* = 0.09) (Figure 5.6). Lattice parameter c continuously decreases from 9.5182Å (*x* = 0) to 9.49514Å (*x* = 0.09). For the Rutile phase, the lattice parameters (*a*, *b*) decrease from 4.593484Å (*x* = 0) to 4.587499 Å (*x* = 0.03) then increases to 4.59114Å (*x* = 0.06) then decreases to 4.58545Å (*x* = 0.09). Lattice parameter c decreases from 2.958896Å (*x* = 0) to 2.954724 Å (*x* = 0.03) then increases to 2.95519Å (*x* = 0.06) and decreases to 2.95406 Å (*x* = 0.09). In the case of Brookite phase lattice parameter a decreases from 5.22941 Å (*x* = 0.06) to 5.1691 Å (*x* = 0.09) while c increases from 5.42374 (*x* = 0.06) to 5.43653(*x* = 0.09). Mn^{3+/4+}

and $V^{3+/4+/5+}$ in titanium oxide lattice introduces enhanced/ lesser coulombic repulsion between metal ions forcing Ti-Ti to increase/ decrease the interatomic distance and balancing it with oxygen ion (coulombic attraction).

For 500° C anatase phase (*a*, *b*) lattice parameters decrease from 3.784487 Å (x = 0.01) Å to 3.784297 Å (x = 0.01) Å, and c parameter decreases from 9.518197 Å to 9.515566 Å. In case of Rutile phase, the lattice parameters (*a*, *b*) decrease from 4.593484Å (x = 0) to 4.590608 Å (x = 0.03) then increase to 4.59455 Å (0.06) and decreases to 4.58956 Å (x = 0.09) (Figure 5.6) the lattice parameters c decreases from 2.958896Å (x=0) to 2.955618 Å (x = 0.03) then increase to 2.95735 Å (x = 0.06) and decreases to 2.95555 Å (x = 0.09). Brookite phase (*a*, *b*) and c lattice parameters remain constant for $0.06 \le x \le 0.09$ as 5.163 Å, 9.159 Å, and 5.4439 Å respectively.

Table 5.2 (a) Results from Rietveld refinement analysis for TVMO, anatase (450 $^{\circ}$ C). The esd's (estimated standard deviations) in the lattice parameters and atomic positions were obtained from GSAS software and is shown in the parenthesis

			TVMO 450C A	ANATASE						
<i>x</i> (a)	Paramet	ters								
0	a (Å) =	3.78449(6) b	(Å) = 3.78449 (6)	c (Å) = 9.51820(2	26)					
l		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy				
	Ti	0	0.25	0.875	0.00338	1.0				
	0	0	0.25	0.08263(14)	0.00471	1.0				
0.01	a (Å) = $3.78422(6)$ b (Å) = $3.78422(6)$ c(Å) = $9.51628(24)$									
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy				
	Ti	0	0.25	0.875	0.01718	0.99				
	0	0	0.25	0.08207(17)	0.01266	1.0				
	V	0	0.25	0.875	0.01928	0.05				
	Mn	0	0.25	0.875	0.02500	0.05				
0.03	a (Å) =	3.78453(5) b	$(\text{\AA}) = 3.78453(5)$	c(Å) = 9.51262(2	2)					
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy				
	Ti	0	0.25	0.875	0.01560	0.97				
	0	0	0.25	0.08290(14)	0.00403	1.0				
	v	0	0.25	0.875	0.025	0.015				
	Mn	0	0.25	0.875	0.025	0.015				
0.06	a (Å) =	3.78558(13)	b (Å) = 3.78558(13	(Å) = 9.51172	2(57)					
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy				
	Ti	0	0.25	0.875	0.00171	0.94				
	0	0	0.25	0.0866(6)	0.01620	1.0				
	V	0	0.25	0.875	0.025	0.03				
	Mn	0	0.25	0.875	0.025	0.03				
0.09	a (Å) =	3.77957(14)	b (Å) = 3.77957(14	4) c (Å) = 9.49514	4(74)					
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy				
	Ti	0	0.25	0.875	0.03439	0.91				
	0	0	0.25	0.077738	0.01108	1.0				
	v	0	0.25	0.875	0.025	0.045				
	Mn	0	0.25	0.875	0.025	0.045				

Table 5.2 (b) Results from Rietveld refinement analysis for TVMO, rutile (450 $^{\circ}$ C) . The esd's(estimated standard deviations) in the lattice parameters and atomic positions were obtainedfrom GSAS software and is shown in the parenthesis

			TVMO 4	50C RUTII	LE	
<i>x</i> (a)	Parame	ters				
0	a (Å) =	4.59370(0) b (Å) = 4.59370(0) c	(Å) = 2.958	370(0)	
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy
	Ti	0	0	0	0.00032	1.0
	0	0.305(8)	0.305(8)	0	0.00032	1.0
0.01	a (Å) =	4.59178(16) b (4	Å) = 4.59178(16)	c(Å) = 2.9	95817(19)	
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy
	Ti	0	0	0	0.01281	0.99
	0	0.3071(12)	0.3071(12)	0	0.00032	1.0
	v	0	0	0	0.03033	0.05
	Mn	0	0	0	0.02500	0.05
0.03	a (Å) =	4.58750(13) b (4	Å) = 4.58750(13)	c(Å) = 2.9	95472(17)	
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy
	Ti	0	0	0	0.03910	0.97
	0	0.3066(9)	0.3066(9)	0	0.00032	1.0
	V	0	0	0	0.02500	0.015
	Mn	0	0	0	0.02500	0.015
0.06	a (Å) =	4.59114(15) b (4	Å) = 4.59114(15)	c (Å) = 2.9	95519(20)	
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy
	Ti	0	0	0	0.00032	0.94
	0	0.3071	0.3071	0	0.00032	1.0
	v	0	0	0	0.02500	0.03
	Mn	0	0	0	0.02500	0.03
0.09	a (Å) =	4.58545(20) b (4	Å) = 4.58545(20)	c(Å) = 2.9	5406(19)	
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy
	Ti	0	0	0	0.00032	0.91
	0	0.3206(18)	0.3206(18)	0	0.00032	1.0
	V	0	0	0	0.02500	0.045
	Mn	0	0	0	0.02500	0.045

Table 5.2 (c) Results from Rietveld refinement analysis for TVMO, brookite (450 $^{\circ}$ C) .The esd's (estimated standard deviations) in the lattice parameters and atomic positions were obtained from GSAS software and is shown in the parenthesis

	TVMO 450C BROOKITE										
<i>x</i> (b)	Parameters										
0.06	a (Å) = 5	a (Å) = 5.22941(1505) b (Å) = 9.08953(2051) c (Å)= 5.42374(940)									
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy					
	Ti	0.4706420	0.1085080	0.0834270	0.05322	0.94					
	01	0.1670750	0.0051320	0.3746680	0.07052	1.0					
	02	0.1321480	0.3030250	0.0417090	0.01904	1.0					
	V	0.3670000	0.1286000	0.1082000	0.025	0.03					
	Mn	0.3670000	0.1286000	0.1082000	0.025	0.03					
0.09	a (Å) = 5.16910(396) b (Å) = 9.13237 (1104) c (Å) = 5.43653(156)										
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy					
	Ti	0.1170250	0.1382180	0.9770150	0.00032	1.0					
	01	0.0190280	0.2224780	0.0507460	0.00032	1.0					
	02	0.2262900	0.1641480	0.4392360	0.00032	0.91					
	V	0.1289000	0.0992000	0.0587030	0.025	0.045					
	Mn	0.1289000	0.0992000	0.8628000	0.025	0.045					

Table 5.2 (d) Results from Rietveld refinement analysis for TVMO, anatase (500 $^{\circ}$ C) .The esd's (estimated standard deviations) in the lattice parameters and atomic positions were obtained from GSAS software and is shown in the parenthesis

			TVMO_500C_	ANATASE								
<i>x</i> (a)	Para	Parameters										
0	a (Å)	a (Å) = 3.78170(5) b (Å) = 3.78170 (5) c (Å) = 9.51421(21)										
		x y z $U_{iso}(Å^2)$ Occupancy										
	Ti	Ti 0 0.25 0.875 0.00338 1.0										
	0	O 0 0.25 0.08357(14) 0.00471 1.0										
0.01	a (Å)) = 3.78430(10)) b (Å) = 3.784	30 (10) c (Å) =	9.51557(4	l6)						
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy						
	Ti	0	0.25	0.875	0.00314	0.99						
	0	0	0.25	0.0840(4)	0.00400	1.0						
	v	0	0.25	0.875	0.00690	0.05						
	Mn	0	0.25	0.875	0.8000	0.05						

Table 5.2 (e) Results from Rietveld refinement analysis for TVMO, rutile (500 $^{\circ}$ C). The esd's (estimated standard deviations) in the lattice parameters and atomic positions were obtained from GSAS software and is shown in the parenthesis

	TVMO 500C RUTILE										
<i>x</i> (a)	Parameters										
0	a (Å) = 4.59222(45) b (Å) = 4.59222(45) c (Å) = 2.95967(66)										
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy					
	Ti	0	0	0	0.00032	1.0					
	0	0.3125(26)	0.3125(26)	0	0.00032	1.0					
0.01	a (Å) = 4	a (Å) = 4.59211(3) b (Å) = 4.59211(3) c (Å) = 2.95762(3)									
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy					
	Ti	0	0	0	0.06191	0.99					
	0	0.30630(25)	0.30630(25)	0	0.03025	1.0					
	V	0	0	0	0.20467	0.05					
	Mn	0	0	0	0.02500	0.05					
0.03	a (Å) = 4.59061(2) b (Å) = 4.59061(2) c (Å) = 2.95562(3)										
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy					
	Ti	0	0	0	0.02671	0.97					
	0	0.3073960	0.3073960	0	0.01441	1.0					
	V	0	0	0	0.02500	0.015					
	Mn	0	0	0	0.02500	0.015					
0.06	a (Å) = 4.59455(6) b (Å) = 4.59455(6) c (Å) = 2.95735(7)										
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy					
	Ti	0	0	0	0.06281	0.94					
	0	0.30714	0.30714	0	0.04720	1.0					
	V	0	0	0	0.02372	0.03					
	Mn	0	0	0	0.02491	0.03					
0.09	a (Å) = 4.58956(5) b (Å) = 4.58956(5) c(Å) = 2.95555(5)										
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy					
	Ti	0	0	0	0.06515	0.91					
	0	0.30478	0.30478	0	0.05031	1.0					
	V	0	0	0	0.33562	0.045					
	Mn	0	0	0	0.07344	0.045					

Table 5.2 (f) Results from Rietveld refinement analysis for TVMO, brookite (500 $^{\circ}$ C). The esd's (estimated standard deviations) in the lattice parameters and atomic positions were obtained from GSAS software and is shown in the parenthesis

	TVMO 500C BROOKITE										
<i>x</i> (b)	Parameters a $(\text{\AA}) = 5.16300(0)$ b $(\text{\AA}) = 9.15900(0)$ c $(\text{\AA}) = 5.43900(0)$										
0.06											
		x	у	z	$U_{iso}(\text{\AA}^2)$	Occupancy					
	Ti	0.3670000	0.1286000	0.1082000	0.05322	0.94					
	01	0.1842000	0.0120000	0.3541000	0.07052	1.0					
	O2	0.0374000	0.2319000	0.1097000	0.01904	1.0					
	v	0.3670000	0.1286000	0.1082000	0.025	0.03					
	Mn	0.3670000	0.1286000	0.1082000	0.025	0.03					
0.09	a (Å) = 5.	a (Å) = 5.16300(0) b (Å) = 9.15900 (0) c (Å) =5.43900(0)									
		x	У	z	$U_{iso}(\text{\AA}^2)$	Occupancy					
	Ti	0.3670000	0.1286000	0.1082000	0.025	0.91					
	01	0.1842000	0.0120000	0.3541000	0.025	1.0					
	O2	0.0374000	0.2319000	0.1-97000	0.025	1.0					
	v	0.3670000	0.1286000	0.1082000	0.025	0.045					
	Mn	0.3670000	0.1286000	0.1082000	0.025	0.045					

5.2.2: Raman spectroscopy:

From the above structural discussion of the materials, it has been established that the co-doping (V/Mn) influences the structural parameters like bond length, tilting angle, crystal symmetry etc. These modifications are important enough to bring in changes in the vibrational properties of the constituent ions. To study these changes, Raman spectroscopy has been performed to explore how the phonon modes get modified due to chemical substitution (co-doping). The changes in atomic positions and chemical bond lengths commensurate with strain that are detected in the Raman spectrum through the changes in peak position or band broadening. The Raman spectra (Figure 5.7)were fitted using multiple peaks corresponding to known phonon modes. Lattice dynamics of the samples for pure TiO₂ (x = 0) was theoretically studied using Density Functional Theory (DFT). Eigenvectors (Vibrational pattern) of the phonon modes obtained from DFT calculations gave a better insight into the detailed lattice dynamics and the microscopic origin of each phonon mode. Experiment values of the phonon frequencies of TiO₂ were compared with simulated results from the DFT calculations.

Bilbao Crystallographic Server is an <u>open access</u> website offering online crystallographic database and programs aimed at analysing and visualizing problems of structural crystallography [51]. From Bilbao sever, one could get the information of how many Raman

active modes are possible in a particular space group by selecting the correct atomic sites of atoms (Table 5.3-5.5)

WP	A _{1g}	A _{1u}	A _{2g}	A _{2u}	B _{1g}	B _{1u}	B _{2g}	B _{2u}	Eu	Eg
4a	•	•	•2	•	1	·		•	•	1
8e	1	•	•	•	1	•	•		•	2

Table: 5.3. Raman active modes of Anatase (space group No. 141: *I4*₁/*amd*, Ti (4*a*) and O(8*e*))

Table: 5.4. Raman active modes of Rutile (space group No. 136: P42/mnm, Ti (2a) and O(4f))

WP	A _{1g}	A _{1u}	A _{2g}	A _{2u}	B _{1g}	B _{1u}	B _{2g}	B _{2u}	Eu	Eg
2a	•	·	•	·	•	•	•	•	·	·
4f	1	•	•	÷	1	•	1	•	•	1

Table: 5.5. Raman active modes of Brookite (space group No. 61: P42/mnm, Ti (8c) and O(8c))

WP	Ag	Au	B _{1g}	B _{1u}	B _{2g}	B _{2u}	B _{3g}	B _{3u}
8c	3	·	3	·	3	•	3	·

These tables provide us the information that Anatase phase has total six Raman active modes at the Γ point (0, 0, 0). $A_{1g} + 2B_{1g} + 3E_g$. Here, *E* represents a doubly degenerate phonon mode, whereas *A* and *B* are nondegenerate phonon modes. A_{1g} is due to the oxygen vibration, one B_{1g} is due to Titanium and second B_{1g} is due to Oxygen vibration. For Rutile phase, total four Raman active modes i.e. $A_{1g} + B_{1g} + B_{2g} + E_g$ and these modes are due to only oxygen vibrations. For Brookite phase, total twelve Raman active modes i.e., $3A_{1g} + 3B_{1g} + 3B_{2g} + B_{3g}$ and these modes are due to both Titanium and Oxygen vibrations.

From DFT simulations, known modes are observed: E_g (1) (131.89 cm⁻¹), E_g (2) (166.08 cm⁻¹), B_{1g} (1) (375.73 cm⁻¹), B_{1g} (2) (476.43 cm⁻¹), A_{1g} (501.75 cm⁻¹), E_g (3) (620.50 cm⁻¹) for Anatase and B_{1g} (142.56 cm⁻¹), E_g (434.87 cm⁻¹), A_{1g} (577.09 cm⁻¹), B_{2g} (786.47 cm⁻¹) for Rutile.



Figure 5.7 Room temperature Raman spectra of TVMO, 450 °C



Figure 5.8 Correlation of Raman Shift with bond length obtained from XRD analysis for TVMO, anatase phase ($450 \,^{\circ}$ C)



Figure 5.9 Correlation of Raman Shift with bond length obtained from XRD analysis for TVMO, rutile phase (450 °C)



Figure 5.10 Room temperature Raman spectra of TVMO, 500 °C



Figure 5.11 Correlation of Raman Shift with bond length obtained from XRD analysis for TVMO, anatase phase (500 °C)



Figure 5.12 Correlation of Raman Shift with bond length obtained from XRD analysis for TVMO, rutile phase (500 °C)

For 450°C annealed samples, the Anatase $I4_1/amd E_g$ (1) at ~ 143.549 cm⁻¹ is due to the vibrations of Ti and two O ions all vibrating along the same direction while third oxygen vibrate in opposite direction. The E_g (1) mode blueshifts from 143.549 cm⁻¹ (TO) to 146.731 cm⁻¹ (TVMO9). The Ti-Ti bond length is observed to decrease with substitution from 3.0402 Å to
3.034 Å. The *I4*₁/*and* E_g (2) at ~ 197 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The E_g (2) mode blueshifts from 197 cm⁻¹ (TO) to 198 cm⁻¹ (TVMO9). The Ti-Ti bond length is observed to decrease with substitution from 3.0402 Å (TO) to 3.034 Å (TVMO9). The *I4*₁/*and* B_{1g} (1) at ~ 399 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The B_{1g} (1) mode redshifts from 399 cm⁻¹ (TO) to 395.852 cm⁻¹ (TVMO1) then blueshifts to 398 cm⁻¹ (TVMO6) further red shifts to 396.527 cm⁻¹ (TVMO9). The Ti-O_P bond length is observed to increase with substitution from 1.9347 Å (TO) to 1.9250 Å (TVMO9). The *I4*₁/*and* A_{1g} at ~ 513 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The A_{1g} mode blueshifts from 513 cm⁻¹ (TO) to 515.937 cm⁻¹ (TVMO9). The Ti-Ti bond length is observed to decrease with substitution from 3.0402 Å (TO) to 3.034 Å (TVMO9). The *I4*₁/*and* E_g (3) at ~ 643 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The E_g (3) mode redshifts from 643 cm⁻¹ (TO) to 639.139 cm⁻¹ (TVMO6) then blueshifts to 639.486 cm⁻¹ (TVMO9). The Ti-O_a bond length is observed to increase with substitution from 1.976 Å (TO) to 2.013 Å (TVMO6) then decrease to 1.9423 Å (TVMO9).

For 450°C annealed samples, the Rutile $P4_2/mnm B_{1g}$ at ~ 140 cm⁻¹ is due to the vibrations of Ti and two O ions all vibrating along the same direction while third oxygen vibrate in opposite direction. The B_{1g} mode blueshifts from 140 cm⁻¹ (TO) to 143.389 cm⁻¹ (TVMO9). The Ti-O_a bond length is observed to decrease with substitution from 1.938 Å to 1.88 Å. The $P4_2/mnm E_g$ at ~ 447.6 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The E_g mode redshifts from 447.6 cm⁻¹ (TO) to 447 cm⁻¹ (TVMO9). The Ti-O_a bond length is observed to increase with substitution from 1.994 Å (TO) to 2.079 Å (TVMO9). The $P4_2/mnm A_{1g}$ at ~612.826 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The A_{1g} mode blueshifts from 399 cm⁻¹ (TO) to 613.9 cm⁻¹ (TVMO3) then redshifts to 612.184 cm⁻¹ (TVMO6) further blueshifts to 612.8 cm⁻¹ (TVMO9). The Ti-Ti bond length is observed to decrease with substitution from 2.9582 Å (TO) to 2.9547 Å (TVMO3) then increase to 2.955 Å (TVFO6) and further slightly decrease to 2.954 Å (TVMO9).

For 500°C annealed samples, the Anatase $I4_1/amd E_g$ (1) [Fig.] at ~ 144.352 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The E_g (1) mode blueshifts from 144.352 cm⁻¹ (TO) to 144.878 cm⁻¹ (TVFO1). The $I4_1/amd E_g$ (2) [Fig.] at ~ 197.071 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The E_g (2) mode blueshifts from 197.071 cm⁻¹ (TO) to 199.014 cm⁻¹ (TVFO1). The $I4_1/amd B_{1g}$ (1) [Fig.] at ~ 395.936 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The B_{1g}

(1) mode redshifts from 395.936 cm⁻¹ (TO) to 391.726 cm⁻¹ (TVMO1). The Ti-O bond length is observed to increase with substitution from 1.984 Å to 1.989 Å. The *I4*₁/amd A_{1g} [Fig.] at ~ 517.701 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The A_{1g} mode blueshifts from 517.701 cm⁻¹ (TO) to 517.445 cm⁻¹ (TVMO1). The Ti-O_a bond length is observed to increase with substitution from 1.984 Å to 1.989 Å. The *I4*₁/amd E_g (3) [Fig.] at ~ 640.891 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The E_g (3) mode redshifts from 640.891 cm⁻¹ (TO) to 641.58 cm⁻¹ (TVMO1).

For 500°C annealed samples, the Rutile $P4_2/mnm B_{1g}$ (Figure 5.10) at ~ 145.274 cm⁻¹ is due to the vibrations of Ti and two O ions all vibrating along the same direction while third oxygen vibrate in opposite direction. The B_{1g} mode redshifts from 145.274 cm⁻¹ (TVMO1) to 138.82 cm⁻¹ (TVMO3) then blueshifts to 141.502 (TVMO9). The Ti-O_p bond length is observed to increase with substitution from 1.9892 Å (TVMO1) to 1.9957 Å (TVMO6) and then decrease to 1.9782 Å (TVMO9). As Rutile phase fraction for TO is less than 2% and hence Rutile peak is not observed. The $P4_2/mnm E_g$ at ~ 447.6 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The E_g mode blueshifts from 447.6 cm⁻¹ (TO) to 447.66 cm⁻¹ (TVMO3) then redshifts to 447 cm⁻¹ (TVMO9). The Ti-O_p bond length is observed to decrease with substitution from 1.9415 Å (TVMO1) to 1.9358 Å (TVMO3) then increases to 1.9466 Å (TVMO9). The $I4_1/amd A_{1g}$ [Fig.] at ~ 612.826 cm⁻¹ is due to the vibrations of Op ions at a small angle parallel to the c-axis. The A_{1g} mode blueshifts from 612.826 cm⁻¹ (TVMO1) to 613.9 cm⁻¹ (TVMO1) then redshifts to 612.8 cm⁻¹ (TVMO9). The Ti-Ti bond length is observed to decrease with substitution from 2.9576 Å (TVMO1) to 2.9556 Å (TVMO3) then increase to 2.9574 Å (TVMO6) and further decrease to 2.9556 Å (TVMO9).

5.2.3: UV-vis spectroscopy:

The optical properties of $Ti_{(1-x)}V_{(x/2)}M_{(x/2)}O_2$ are observed using UV-Visible absorption spectra. The electronic band gap is estimated using Tauc equation [30].

Bandgap plot (Figure 5.13) reveals that bandgap continuously decreases with V/Mn co-doping for both 450°C and 500°C annealed samples. Anatase and Rutile phase bandgap was found to decrease from 2.89 eV to 1.03 eV and 3.105 eV to 1.94 eV respectively for TVFO 450°C annealed samples. For TVMO 500°C annealed samples, Anatase and Rutile phase bandgap was found to decrease from 2.914 eV (x = 0) to 1.323 eV (x = 0.01) and 3.204 eV to 1.852 eV respectively. The values of bandgap for TiO₂ for Anatase and Rutile phase are comparable to literature. Band structure (TiO₂) for both Anatase and Rutile obtained by DFT simulation reveals that the valence band maxima is majorly dominated by the O-states and conduction band minima dominated by the Ti-states. An indirect and direct bandgap is observed for Anatase and Rutile respectively. The electronic transitions mainly occur between $\Gamma VB \rightarrow \Gamma CB$. DFT calculated bandgap value is closer to experimental value and other reports as discussed in previous chapter.



Figure 5.13 UV-Vis spectra of TVMO for anatase and rutile phase (450°C and 500°C)



Figure 5.14 Variation of band gap and urbach energy with composition, x for TVMO, anatase and rutile phase (450 °C and 500 °C)

Hence, increase in the Ti-O bond strength for 450°C and 500°C annealed samples of Anatase phase highly reflect modifications of Eg. Interestingly, the Ti-O bond length decreases from 1.935 Å (x = 0) to 1.925 Å (x = 0.09) for 450°C and decreases from 1.984 Å (x = 0) to 1.955 Å (x = 0.01) for 450°C and 500°C respectively i.e., becomes stronger x. Similar trend is observed for the Raman mode Eg(1) which represents tilting. Strong hybridization/ overlapping of orbitals between Ti_{3d} and O_{2p} states can visualized by increase in \angle TiOTi with x. For Rutile phase, the Ti-O bond length overall shows decreasing trend from 1.95 Å (x = 0) to 1.88 Å (x =0.09) for 450°C and 2.029 Å (x = 0) to 1.978 Å (x = 0.09) for 450°C and 500°C respectively. Also, overall increasing trend is observed for 450°C and 500°C anneal \angle TiOTi with x.

However, it is noteworthy, that the width of defect bands, generally related to the strained electronic states are related to the Urbach tail states. The Urbach energy, E_u , can be expressed as a $\alpha = \alpha_0 \exp(h\nu/E_u)$ [79]; where, α_0 is a constant. Eu can be estimated by modifying the above relation as $\ln (\alpha) = \ln \alpha_0 + (h\nu/E_u)$. These states are extremely localized and characterize individual disordered states in a system. Interestingly, E_u continuously increases with V/Mn

co-doping for both 450°C and 500°C annealed samples (Figure 5.14). Urbach energy plotreveals that E_u continuously decreases with V/Mn co-doping for both 450°C and 500°C annealed samples. Anatase and Rutile phase E_u was found to increase from 0.625 to 1.102 and 0.2 to 0.4723 respectively for TVFO 450°C annealed samples. For TVFO 500°C annealed samples, Anatase and Rutile phase Eu was found to increase from 0.1654 to 0.289 and 0.465 to 0.5697 respectively. Due, to oxygen related defect states width increases with *x*.

Chapter 6

CONCLUSIONS

Rietveld analysis of room temperature XRD data of TVFO samples annealed at 450 °C shows a mixed phase i.e., Anatase and Rutile for $0 \le x \le 0.09$. A mixed phase, Anatase and Rutile for $0 \le x \le 0.01$ and single phase (Rutile) for $0 \le x \le 0.01$ for 500 °C. In case of TVMO (450 °C), a mixed phase i.e., Anatase and Rutile for $0 \le x \le 0.03$ and Anatase, Rutile and Brookite for $0.06 \le x \le 0.09$. TVMO (500 °C), a mixed phase i.e., Anatase and Rutile for $0 \le x \le 0.01$, single phase (Rutile) for x = 0.03 and Rutile and Brookite for $0.06 \le x \le 0.09$. Appearance of Brookite phase in TVMO samples annealed at 450 °C and 500 °C reveal that repulsive force between Tisite and Ti-site increases due to average higher charge with the incorporation of V⁵⁺/Mn⁴⁺. To counter part this repulsive force, Ti-Ti separation distances increases which results in orthorhombic phase.

Displacement pattern corresponding to each phonon modes has been correlated with the experimental shifts and bond length. The structural arrangement controls the octahedral distortion/tilting and plays a key role in tuning the phase and electronic properties of TVFO and TVMO. Correlation of structural properties with vibrational and electronic properties has been proposed in this work. Raman mode Eg(1) of Anatase which corresponding to tilting angle has strong dependence on electronic properties. With V/Fe and V/Mn results in decrement of band gap and increment of urbach energy. Oxygen related defect state band increases with these co-doping. DFT simulated Band structure at gamma point shows direct band gap for Rutile and indirect band-gap for anatase. Tuning of band gap from UV range to visible range was possible with V/Mn co-doping as compared to V/Fe co-doping. The theoretical magnetic moments for the Fe³⁺ and the Mn³⁺ ions are 5 Bohr magneton and 4 Bohr magneton respectively. The different d- electron environments in FeO₆ and MnO₆ octahedral units leads different crystal field splitting between t_{2g} and e_g levels which modifies the extent of overlapping of Ti and O orbital.

APPENDIX

	2						-	\sim	~
IО	2	P	U	ĸ	E	4	5	U	L

Lattice parameters	Lattice constant Standard devia	ts are 3.78449 ations 0.00006	3.78449 0.00006	9.51820 0.00026	
Atomic positions	Til 0.000 01 0.000	0000(0) 0.250000 0000(0) 0.2500000	0(0) 0.875 0(0) 0.082	60000(0) 263(14)	
Bond Length	Vector Til_Til Til_Til Til_Til Til_Til Til_Ol Til_Ol Til_Ol Til_Ol Til_Ol Til_Ol	Length 3.04020(5) 3.04020(5) 3.04020(5) 1.9763(13) 1.93474(27) 1.93474(27) 1.93474(27) 1.93474(27) 1.93474(27) 1.93474(27) 1.93474(27)			Fitted wRp 0.0489 0.(CHI**2 =
	Vector O1_Ti1 O1_Ti1 O1_Ti1	Length 1.9763(13) 1.93474(27) 1.93474(27)			
		Anatase			

Bond Angle

Anatase

Angle 01_Ti1_01 01_Ti1_01 01_Ti1_01 01_Ti1_01	Degrees 102.03(4) 102.03(4) 77.97(4) 77.97(4)		
Ol_Ti1_O1 Ol_Ti1_O1 Ol_Ti1_O1 Ol_Ti1_O1 Ol_Ti1_O1 Ol_Ti1_O1 Ol_Ti1_O1 Ol_Ti1_O1 Ol_Ti1_O1 Ol_Ti1_O1 Ol_Ti1_O1 Ol_Ti1_O1 Ol_Ti1_O1	180.000(0) 155.94(8) 92.490(15) 92.490(15) 77.97(4) 92.490(15) 92.490(15) 77.97(4) 155.94(8) 102.03(4) 102.03(4)	Angle Ti1_01_Ti1 Ti1_01_Ti1 Ti1_01_Ti1	Degrees 102.03(4) 102.03(4) 155.94(8)

1.673

Rutile Lattice parameters Lattice constants are Standard deviations 4.59370 4.59370 2.95870 Atomic positions Ti 0.0000000(0) 0.000000(0) 0.000000(0) 0.305(8) 0.305(8) 0.0000000(0) 0.0000000(0)

Bond Length	Vector Ti_Ti Ti_Ti Ti_O Ti_O Ti_O Ti_O Ti_O Ti	Length 2.95870(0) 2.95870(0) 1.98(6) 1.95(4) 1.95(4) 1.95(4) 1.95(4) 1.95(4)
	Vector O_Ti O_Ti O_Ti	Length 1.98(6) 1.95(4) 1.95(4)

Anatas	e	TVF	O_0P01_4	50C	Vector Til_Til	Length 3.04058(10)
Lattice parame	ters			Fitted	Til_Til Til_Til	3.04058(10) 3.04058(10)
Lattice const Standard de Atomic positio	ants are viations ons	3.78531 3.78531 0.00011 0.00011	9.51878 0.00051	wRp Rp 0.0600 0.0466 CHI**2 = 2.852	Ti1_01 Ti1_01 Ti1_01 Ti1_01 Ti1_01 Ti1_01	1.9807(27) 1.9343(6) 1.9343(6) 1.9343(6) 1.9343(6) 1.9343(6)
Til 0.0 01 0.0 V 0.0 Fe 0.0	000000 (0) 000000 (0) 000000 (0) 000000 (0)	0.2500000(0) 0.8 0.2500000(0) 0.08 0.2500000(0) 0.8 0.2500000(0) 0.8	750000 (0) 3308 (29) 750000 (0) 750000 (0)		Ti1_U Ti1_V Ti1_V Ti1_V Ti1_V Ti1_V	1.9807(27) 3.04058(10) 3.04058(10) 3.04058(10) 3.04058(10) 3.04058(10)
			Vector V_Til V_Til V_Til	Length 3.04058(10) 3.04058(10) 3.04058(10)	Til_Fe Til_Fe Til_Fe Til_Fe	3.04058 (10) 3.04058 (10) 3.04058 (10) 3.04058 (10)
Bond Length	Vector Fe_Til Fe_Til Fe_Til Fe_O1 Fe_O1 Fe_O1 Fe_O1 Fe_O1 Fe_O1 Fe_O1	Length 3.04058 (10 3.04058 (10 3.04058 (10 3.04058 (10 1.9807 (27) 1.9343 (6) 1.9343 (6) 1.9343 (6) 1.9343 (6) 1.9807 (27)	V_Til V_Til V_01 V_01 V_01 V_01 V_01 V_01 V_01 V_01 V_01 V_01 V_V V_V V_V V_V V_V V_V	3.04058 (10) 1.9807 (27) 1.9343 (6) 1.9343 (6) 1.9343 (6) 1.9343 (6) 1.9807 (27) 3.04058 (10) 3.04058 (10) 3.04058 (10)	Vector 01_Ti1 01_Ti1 01_Ti1 01_V 01_V 01_V 01_V 01_Fe 01_Fe 01_Fe	Length 1.9807 (27) 1.9343 (6) 1.9343 (6) 1.9807 (27) 1.9343 (6) 1.9807 (27) 1.9343 (6) 1.9343 (6) 1.9343 (6)

Anatase Bond Angle 01_Ti1_01	Degrees 101.90(8) 101.90(8)	Angle Til_01_Ti1 Ti1_01_Ti1 Ti1_01_V Ti1_01_V Ti1_01_V Ti1_01_Fe Ti1_01_Fe Ti1_01_Fe	Degrees 101.90(8) 101.90(8) 0.000(0) 101.90(8) 101.90(8) 0.000(0) 101.90(8) 101.90(8)	Ang Til_01 Til_01 Til_01 Til_01 Til_01 Til_01 Til_01 Til_01 Til_01 Til_01 Til_01 Til_01	1e 	Degrees 156.19(16) 0.000(0) 156.19(16) 0.000(0) 156.19(16) 156.19(16) 156.19(16) 156.19(16) 156.19(16) 156.19(16) 101.90(8) 155.19(16)
01_Ti1_01 01_Ti1_01 01_Ti1_01 01_Ti1_01 01_Ti1_01 01_Ti1_01 01_Ti1_01	78.10(8) 78.10(8) 180.000(0) 156.19(16) 92.439(32) 92.439(32)	V_01_V V_01_V V_01_Fe V_01_Fe V_01_Fe V_01_V V_01_Fe	101.90(8) 101.90(8) 0.000(0) 101.90(8) 101.90(8) 156.19(16)	111_01 V_01 V_01 V_01 V_01 V_01 V_01 V_0	V Fe Fe Fe Fe	0.000(0) 101.90(8) 101.90(8) 101.90(8) 101.90(8) 101.90(8) 156.19(16) 101.90(8) 0.000(0)
01_Ti1_01 01_Ti1_01 01_Ti1_01 01_Ti1_01 01_Ti1_01 01_Ti1_01 01_Ti1_01 01_Ti1_01	78.10(8) 92.439(32) 92.439(32) 78.10(8) 156.19(16) 101.90(8) 101.90(8)	V_01_Fe V_01_Fe V_01_Fe V_01_Fe V_01_Fe Fe_01_Fe Fe_01_Fe Fe_01_Fe Fe_01_Fe	101.90(8) 0.000(0) 156.19(16) 101.90(8) 156.19(16) 0.000(0) 101.90(8) 101.90(8) 156.19(16)	Angle 01_Fe_01 01_Fe_01 01_Fe_01 01_Fe_01 01_Fe_01 01_Fe_01		Degrees 101.90(8) 101.90(8) 78.10(8) 78.10(8) 180.000(0) 156.19(16)
Angle 01_V_01 01_V_01 01_V_01 01_V_01 01_V_01	Degrees 92.439(32) 78.10(8) 156.19(16) 101.90(8) 101.90(8)	Angle o1_V_01 o1_V_01 o1_V_01 o1_V_01 o1_V_01 o1_V_01 o1_V_01 o1_V_01 o1_V_01 o1_V_01 o1_V_01 o1_V_01	Degrees 101.90(8) 101.90(8) 78.10(8) 78.10(8) 180.000(0) 156.19(16) 92.439(32) 92.439(32) 78.10(8) 92.439(32)	OI_Fe_OI OI_Fe_OI OI_Fe_OI OI_Fe_OI OI_Fe_OI OI_Fe_OI OI_Fe_OI OI_Fe_OI		92.439(32) 92.439(32) 78.10(8) 92.439(32) 92.439(32) 78.10(8) 156.19(16) 101.90(8) 101.90(8)
			52.105 (52)			
Anatase		TVFO_0P03	_450C	Vecto Fe_T: Fe_T:	or i1 i1	Length 3.04018(9) 3.04018(9)
Lattice parameters				re_1.	11	3.04010(9)

Latt St	tice constants ar candard deviation	e 3.78524 s 0.00010	3.78524 0.00010	9.51687 0.00043	Fitted wRp Rp 0.0582 0.0438 CHI**2 = 2.826	Fe_Til Fe_O1 Fe_O1 Fe_O1 Fe_O1 Fe_O1 Fe_O1 Fe_O1	3.04018(9) 1.9769(23) 1.9349(5) 1.9349(5) 1.9349(5) 1.9349(5) 1.9349(5) 1.9769(23)
Til Ol V Fe	0.0000000 (0 0.0000000 (0 0.0000000 (0 0.0000000 (0 Bond Length Vector 01_Til 01_Til) 0.2500000(0) 0.2500000(0) 0.2500000(0) 0.2500000(0) Length 1.9769(23) 1.9349(5)) 0.8750) 0.0827) 0.8750) 0.8750	000(0) 2(24) 000(0) 000(0) Vector V_Til V_Til V_Til V_Til V_Til V_Ol	Length 3.04018 (9) 3.04018 (9) 3.04018 (9) 3.04018 (9) 1.9769 (23)	Vector Ti1_Ti1 Ti1_Ti1 Ti1_Ti1 Ti1_O1 Ti1_O1 Ti1_O1 Ti1_O1 Ti1_O1 Ti1_O1 Ti1_O1	Length 3.04018(9) 3.04018(9) 3.04018(9) 3.04018(9) 1.9769(23) 1.9349(5) 1.9349(5) 1.9349(5) 1.9349(5)
	01_Ti1 01_V 01_V 01_V 01_Fe 01_Fe 01_Fe	1.9349(5) 1.9769(23) 1.9349(5) 1.9349(5) 1.9769(23) 1.9349(5) 1.9349(5)		V_01 V_01 V_01 V_01 V_01 V_0 V_V V_V V_V V_V V_V	1.9349(5) 1.9349(5) 1.9349(5) 1.9349(5) 1.9769(23) 3.04018(9) 3.04018(9) 3.04018(9)	Ti1_01 Ti1_V Ti1_V Ti1_V Ti1_V Ti1_Fe Ti1_Fe Ti1_Fe Ti1_Fe Ti1_Fe	1.9769(23) 3.04018(9) 3.04018(9) 3.04018(9) 3.04018(9) 3.04018(9) 3.04018(9) 3.04018(9) 3.04018(9) 3.04018(9)

Rutile Bond Angle	Angle Ti_O_Ti Ti_O_V Ti_O_V Ti_O_V Ti_O_V Ti_O_Fe Ti_O_Fe Ti_O_Fe Ti_O_V Ti_O_V Ti_O_V Ti_O_V Ti_O_V Ti_O_Fe Ti_O_Fe Ti_O_Fe	Degrees 130.57(5) 130.57(5) 0.000(0) 130.57(5) 130.57(5) 130.57(5) 98.86(10) 130.57(5) 0.000(0) 98.86(10) 130.57(5) 0.000(0) 130.57(5) 0.000(0)	Angle O_Ti_O	Degrees 90.000(0) 90.000(0) 180.000(0) 90.000(0) 98.86(10) 90.000(0) 81.14(10) 180.000(0) 90.000(0) 180.000(0) 81.14(10) 90.000(0) 90.000(0) 98.86(10)	Angle Ti_O_Fe Ti_O_V Ti_O_V Ti_O_Fe Ti_O_Fe Ti_O_Fe V_O_V V_O_V V_O_V V_O_Fe	Degrees 98.86(10) 130.57(5) 98.86(10) 0.000(0) 130.57(5) 98.86(10) 0.000(0) 130.57(5) 130.57(5) 130.57(5)
	Angle 0. V.0 0. V.0	Degrees 90.000(0) 90.000(0) 180.000(0) 90.000(0) 90.000(0) 98.86(10) 90.000(0) 81.14(10) 180.000(0) 90.000(0) 180.000(0) 81.14(10) 90.000(0) 90.000(0) 98.86(10)	Angle 0_Fe_0	Degrees 90.000(0) 90.000(0) 180.000(0) 90.000(0) 98.86(10) 90.000(0) 81.14(10) 180.000(0) 90.000(0) 81.14(10) 90.000(0) 81.14(10) 90.000(0) 90.000(0) 98.86(10)	V_0_Fe V_0_Fe V_0_Fe V_0_Fe V_0_Fe V_0_Fe V_0_Fe V_0_Fe Fe_0_Fe Fe_0_Fe Fe_0_Fe	130.57(5) 98.86(10 130.57(5) 0.000(0 98.86(10 130.57(5) 98.86(10 0.000(0 130.57(5) 130.57(5) 98.86(10

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