LIGHT-INDUCED TRANSFORMATION OF
NANOSTRUCTURED V₃O₇·H₂O TO V₂O₅

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2006

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
May, 2010
LIGHT-INDUCED TRANSFORMATION OF
NANOSTRUCTURED $V_5O_7\cdot H_2O$ TO $V_2O_5$

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ACKNOWLEDGMENTS

First and foremost, I would like to express my gratitude to my adviser, Dr. A. Kaan Kalkan, for his patience, encouragement, and warmhearted guidance and support throughout my Masters studies. I am grateful to him for inspiring me by his endless enthusiasm, and passion for science and research. I would also like to thank to the members of my thesis committee Dr. Raman Singh and Dr. Sandip Harimkar for their valuable time, and feedback.

I would like to extend my sincere thanks to Dr. Hongbing Lu, Dr. Nicholas Leventis, and Gitogo Churu for providing us with information on vanadium oxide aerogel preparation technique. I would also express my gratitude to Dr. Jay Hanan, Dr. Alejandro Rodríguez Navarro from University of Granada in Spain and Masoud Allahkarami for their help on X-Ray diffraction studies.

I want to express my acknowledgements to Dr Susheng Tan and Terry Colberg for their help on SEM. My sincere thanks also go to the members of the Functional Nanomaterials Laboratory for their friendship and support.

Finally, I would like to thank to my parents, my brother, my sister and my boyfriend for their unflagging understanding, support, encouragement and love.
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CHAPTER 1
INTRODUCTION

Transition metals are the elements with incomplete d electron shells. One interesting attribute of transition metals is that they exhibit variety of oxidation states. Consequently, they can form several single valence, and mixed valence oxides. Due to this diversity in chemistry, transition metal oxides can exhibit chemical and structural transformations under the influence of different external factors, such as electron and ion bombardment, heat treatment, and electromagnetic radiation [1]. Further, transition metal oxides have the ability to influence the reduction and oxidation processes finding uses as catalysts, and catalytic supports [2]. Transition metal oxides also serve as electrode materials in certain electrochemical devices. In addition, they are utilized in electronics industry as transparent conducting oxides or active semiconductor layers [3].

In the present thesis work, light induced phase transformation of a transition metal oxide has been observed and studied. This phase transformation occurs between two different oxides of vanadium, prepared by sol-gel chemistry, namely from V₃O₇·H₂O to V₂O₅, under laser irradiation as low as ≅0.31 kW/cm². An interesting feature of this phase
transformation is found to be its athermal origin.

Some of the vanadium oxides, such as VO$_2$ and V$_6$O$_{13}$, undergo a metal to semiconductor phase transition involving change in crystal structure at certain temperatures. This property of vanadium oxides provides an opportunity for numerous electrical and optical applications, such as optical and electrical switches, optical memory, thermistors, and reflectors [4-6].

In addition, amorphous to crystalline transition in V$_2$O$_5$ was reported by Witke et al. by a 514.5 nm argon ion laser at 63.6 kW/cm$^2$ power density. The same group also demonstrated laser induced oxidation of V$_4$O$_9$ to V$_2$O$_5$ by 514.5 nm laser irradiation of 190.8 kW/cm$^2$. They attributed this transformation to a thermal effect [7]. Further, Liu et al. observed laser induced coloration of V$_2$O$_5$ (i.e., from pink yellow to dark blue) upon 308 nm XeCl excimer laser irradiation of $3.47 \times 10^6$ W/cm$^2$. They attributed this coloration to a laser induced creation of defects (i.e., thermochromism) [8].

The present work investigates the light induced V$_3$O$_7$·H$_2$O to V$_2$O$_5$ transformation by Raman spectroscopy. This investigation was carried out in both air and Ar ambient. Raman spectroscopy was also employed to rule out the heating effects and measure the temperature during this transformation which is as low as 25-29 °C (i.e., measurements performed at room temperature). In contrast, it is observed by Zakharova et al. that the same transformation occurs at 400 °C when it is driven thermally by annealing samples for 30 minutes [9]. Further, the present work explored kinetics of the light-induced V$_3$O$_7$·H$_2$O to V$_2$O$_5$ transformation by photoluminescence.
The organization of the present thesis is as follows. In Chapter 2, the background on properties and certain applications of vanadium oxides is reviewed. In Chapter 3, procedures for vanadium oxide aerogel preparation and characterization methods utilized are described. Chapter 4 presents the results. In particular, Raman scattering was used to monitor the phase transformation and measure the temperature during the transformation. In addition, the kinetics of the phase transformation as probed by photoluminescence is discussed. Electron microscopy images and X-ray diffraction data are provided for the elucidation of nanostructure and crystal structure. Finally, Chapter 5 concludes the present study, and suggests directions for future research.
CHAPTER 2
BACKGROUND

Vanadium is a transition metal which is found in several different minerals, iron ores, as well as in crude oil deposits. V was first discovered by A.M. del Rio, a Spanish mineralogist, in 1801 and named as erythronium. The element then was declared and had been known as an impure form of chromium until it was rediscovered in 1830 by Swedish chemist N.G. Sefström. Sefström named this new element vanadis, the nickname of Scandinavian fertility and love goddess Freyja [10, 11].

Vanadium has different variety of metallurgical applications. A most common application of vanadium is as an additive to improve shock and vibration resistance of steel. Vanadium also finds wide applications in aerospace industry in, such as jet engines and high-speed airframes. When mixed in titanium alloys with aluminum, vanadium increases titanium’s strength, and resistance to high operating temperatures and stress. In addition, vanadium salts are used in ceramics and textile dyes due to their bright colors [11].

Vanadium exhibits main oxidation states of +2, +3, +4 and +5 in its oxides with variety of crystal structures. There are four single valence oxides of vanadia which
consist of ions with the same valence charge, \(\text{VO}, \text{V}_2\text{O}_3, \text{VO}_2\), and \(\text{V}_2\text{O}_5\). In addition, there are certain oxidation states of vanadia where ions of different valence charges present at the same time called mixed valence oxides. Examples of these oxides are \(\text{V}_n\text{O}_{2n-1}\) and \(\text{V}_n\text{O}_{2n+1}\) Magneli phases with \(2 \leq n \leq 9\) [12]. Due to this diversity in chemistry, vanadium oxides offer physical, chemical, and electronic properties which find use in a wide range of applications in, such as gas sensors, lithium insertion electrodes, catalysts and optical switches [13-15].

Vanadium oxides are generally used as catalysts. Typically, vanadium oxides are used to catalyze certain oxidation processes, such as oxidation of \(\text{SO}_2\) to \(\text{SO}_3\), naphthalene or \textit{ortho}-xylene to phthalic anhydride, and n-butane to benzaldehyde. In recent years, vanadium oxide catalysts also have been used in the reduction of \(\text{NO}_x\) [11, 16]. Besides oxidation and reduction of various chemicals, this group of catalysts is also exploited in gas sensing. As an example, reducing gases such as \(\text{SO}_2\) and hydrocarbons can be detected by vapor deposited \(\text{V}_2\text{O}_5\) films on the basis of electrical conductivity change [17].

\(\text{V}_2\text{O}_5\) is an attractive material as a counter electrode for Li batteries due to its low cost, high energy density, easy synthesis, and high stability. The performance of \(\text{V}_2\text{O}_5\) cathodes highly depends on the crystallinity. Consequently, there have been many studies on improving the performance of these cathodes (e.g., better specific capacity and cyclability) by modifying the structure. A number of studies have shown that crystalline \(\text{V}_2\text{O}_5\) cathodes exhibits high specific capacity, but the cyclability is substantially weak because of the structural damage during the cycles. However, amorphous and low crystalline \(\text{V}_2\text{O}_5\) have high Li-ion diffusion rate, and significant cyclability [18].
Morphology is another important parameter for the performance of the cathode materials. Lately, nanostructured cathode materials have become popular owing to their enhanced capacity and cyclability. This enhancement in performance results from size effects including high surface to volume ratio, and changes in the energy distribution of electronic states. In particular, highly porous nanostructures, e.g., aerogels, would be ideal candidates as the cathode for high performance Li batteries, because the electrolyte would easily penetrate into the material, and also the distance which the intercalated ions travel is reduced [18, 19].

Vanadium oxides can exhibit different electronic properties. Some of the vanadium oxides show metallic characteristics, such as V$_2$O$_3$ and V$_7$O$_{13}$, whereas some of them are semiconductors, such as V$_2$O$_5$, V$_3$O$_7$, and V$_4$O$_9$. In addition, some of the vanadium oxides undergo a reversible metal to semiconductor phase transition. Examples of these oxides are VO$_2$, and V$_6$O$_{13}$ which exhibit metal to semiconductor phase transition at 340 and 150 K, respectively [4]. The metal to semiconductor transition in vanadium oxides occur along with a change in crystal structure. For example, crystal structure of VO$_2$ changes from monoclinic to tetragonal while it transforms from semiconductor to metal [4]. Besides a change in the electronic properties, a dramatic change in optical properties also occurs through this phase transformation that opens the door to optical switching [5].

Another attractive property of the vanadium oxides are the photochromism, and electrochromism. Photochromism, or electrochromism is the ability of a material to change its optical absorption when exposed to an optical excitation, or an electric field [20, 21]. After the exposure is removed, the coloration remains, but it can be reversed
when another optical source, or reversed electric field is applied. This feature of vanadium oxides makes them proper candidates in applications, such as information displays, and optical switches [21].

The reason behind the coloration of these materials is the trapping of electrons in certain lattice sites (i.e., midgap electronic states) that changes the visible light absorption of the material. In the photochromic case, these trapped electrons are provided internally from the material itself (i.e., valence band). However, in the case of electrochromism, electrons are provided externally by an applied electric field [21].

In addition to photochromism and electrochromism, coloration in vanadium oxides can occur due to a photo-induced thermochromism [20]. Laser induced coloration, crystallization, and oxidation of certain vanadium oxides have been studied by different groups [7, 8, 22]. Liu et al. demonstrated laser-induced coloration of \( \text{V}_2\text{O}_5 \) pellets under 308 nm XeCl excimer laser with \( 3.47 \times 10^6 \) W cm\(^{-2} \) energy density. They showed that samples were changed color from pink yellow to dark blue along with an increase in conductivity. Originally, \( \text{V}_2\text{O}_5 \) is a semiconductor at room temperature, whereas the colored samples have electrical resistivity in the order of \( 10^3 \) \( \Omega \) cm. They attributed this coloration to a laser induced thermochromism. In their X-ray diffraction and Raman spectroscopy measurements, they observed that the samples were sub-stoichiometric with an oxygen deficiency, but the crystalline structure was the same as the uncolored samples [8].

In another study, Witke et al. showed the laser-induced crystallization of potentiodynamically produced amorphous vanadium oxide thin films by a 514.5 nm
argon ion laser at 63.6 kW/cm$^2$ power density. In the same study, they also demonstrated laser-induced oxidation of V$_4$O$_9$ thin films with addition of V$_2$O$_5$ phase to V$_2$O$_5$ at 190.8 kW/cm$^2$ power density [7].

There are several vanadium oxide hydrates consisting of +5 and +4 oxidation states. V$_3$O$_7$·H$_2$O is one of the most attractive oxides in this group of materials due to its promising electrochemical and catalytical properties. In particular, different types of nanostructured V$_3$O$_7$·H$_2$O, such as nanobelts, nanofibers, and nanowires, have received great attention, and their structures and electrochemical properties have been studied [9].

As described by Oka et al., structure of vanadium oxide hydrate is layered consisting of two types of VO$_6$ octahedra (V(1) O$_6$ and V(2) O$_6$) and one type of VO$_5$ trigonal bipyramid. In this structure, a V(1) O$_6$ and a V(2) O$_6$ octahedron share edges, and form piles along the c axis. Further, two VO$_5$ trigonal bipyramids sharing edges along the b axis connect these VO$_6$ piles and form V$_3$O$_8$ layers along the a axis (Fig. 2.1a). The V$_3$O$_8$ layers are hold together by water molecules which replace one of the oxygen atoms in a VO$_6$ octahedron in one layer and form hydrogen bond with a VO$_6$ octahedron in another layer [9, 23]. According to our understanding, water molecule is bound to a VO$_6$ octahedron by forming a coordinate bond between oxygen and vanadium where the shared electrons come from oxygen as shown in Fig. 2.1b. This model explains how a vanadium atom can make bonds with six oxygen atoms while its highest oxidation state is +5.
**Figure 2.1:** a) Crystal structure of V$_3$O$_7$·H$_2$O. The sketch is inspired from Oka *et al.* [23]. The dots represent V atoms. b) Model illustrating the coordinate bonds between vanadium and oxygen in water. The model also shows how V$_3$O$_8$ sheets are hold together by hydrogen bonds.

V$_2$O$_5$ has a structure similar to V$_3$O$_7$·H$_2$O. It is orthorhombic with a corrugated sheet type (layered) structure at room temperature. The basic unit is a distorted trigonal bipyramid in which vanadium atom is surrounded by three types of oxygen; vanadly (O$^1$), chain (O$^2$), and bridge (O$^3$). In this basic unit, due to the distinct displacements of vanadium atoms in [VO$_6$] octahedron, the basic unit turns into VO$_5$ square pyramid as seen Fig. 2.2. The sheet structure is formed by these distorted bipyramids sharing edges and corners [24]. Further, V$_2$O$_5$ is yellow-orange colored with a band gap of 2.2-2.3 eV as reported by different groups [25, 26].
Figure 2.2: $\text{V}_2\text{O}_5$ crystal structure (the copyright holder of this work releases it into the public domain; http://en.wikipedia.org/wiki/File:Vanadium-pentoxide-monolayer-3D-balls.png , January 7, 2010).
CHAPTER 3

METHODOLOGY

3.1. Materials and Sample Preparation

3.1.1. Precursor Materials

Vanadium (V) tripropoxide (VO (OCH₂CH₂CH₃)₃) was purchased from Sigma Aldrich, Inc. Acetone (HRGC/HPLC grade) was purchased from Pharmco-AAPER Alcohol and Chemical, Inc. Both chemicals were used as received. Deionized water (18.2 MΩ cm) was obtained from an Elga Purelab Ultra water purification system. Siphon grade CO₂ was purchased from Stillwater Steel and Supply, LLC, Stillwater, OK.

3.1.2. Synthesis of Aerogels

In the present study, V₂O₇·H₂O aerogels were prepared by supercritical drying of wet vanadia gels obtained via modification of Dunn’s procedure as indicated in the paper of Leventis et al.[27] In this process, a mixture of 5.58 ml of deionized water and 11.34 ml of acetone was added to 2.4 ml of vanadium(V) tripropoxide, VO(OCH₂CH₂CH₃)₃.

In order to slow down the gelation process, the liquid precursors (i.e., as described above) were cooled in a CO₂ ice/acetone bath (-78 °C) until ice appeared in water/acetone
mixture and vanadium (V) tripropoxide became more viscous. Prior to the mixing, water/acetone mixture was shaken vigorously until ice chunks disappeared. The water/acetone mixture was subsequently added into vanadium (V) tripropoxide at once. The obtained mixture (sol) was shaken for 10-15 seconds and transferred to the polyethylene syringes (Becton Dickinson & Co., Luer-LokTM Tip, 5 ml) immediately while it was still cold, and sealed with Parafilm. Samples were aged for five days in their molds (syringes). After aging, gels were removed from the syringes and placed into a jar filled with anhydrous acetone, approximately 4-5 times the total gel volume. The acetone was changed periodically, once every 24 hours for four times. After the water inside the aerogels was fully exchanged with acetone, supercritical drying with CO$_2$ was performed to remove the acetone. Figure 3.1 shows the preparation steps of vanadium aerogels.

![Figure 3.1. Schematics of vanadia aerogel preparation.](image)

### 3.1.3. Critical Point Drying of Aerogels

Drying process is the most critical step in the aerogel preparation. Aerogels prepared by the method described in Section 3.1.2 are highly porous and fragile [27]. Drying of samples in air, results in collapse of the pores due to the capillary forces.
Therefore, the acetone in the aerogel was removed by critical point drying (CPD) without any damage to the structure.

As the liquid evaporates, the samples are subject to capillary forces present at the phase boundary. However, at critical point, a fluid and its vapor phase coexist and the surface tension between these two phases becomes zero. If the temperature and the pressure are kept above the critical point, super critical fluid can be released without harming the structure of the samples [28].

In the present study, critical point drying of aerogels was performed by Quorum Technologies E3100 Series critical point dryer. Samples were placed on the sample holder of the dryer, and the sample holder was placed into the pressure chamber of the system. The system was pre-cooled to 20 °C by running cold water. In order to prevent air drying, the dryer chamber was filled with acetone initially. Subsequently, the access door was closed tightly, and the supply valve of the gas cylinder was opened. The inlet valve was opened fully to fill the chamber with liquid gas. Samples were left in the liquid CO$_2$ for 20 minutes to allow the penetration of the liquid CO$_2$ into the samples. The substitution liquid was then drained through the drain valve. This flushing step was repeated for 8-10 times until the acetone was completely replaced with liquid CO$_2$.

Subsequent to the flushing steps, the chamber was filled with liquid CO$_2$ until the liquid reached to the top of the chamber. At this point, temperature of the liquid CO$_2$ was around 18 °C, and the pressure inside the chamber was approximately 955 Psi (65 Atm). The inlet valve was closed and the hot water supply was turned on to increase the temperature of the chamber. The chamber was observed through the viewing window,
while the temperature and pressure gauges were being monitored. After CO₂ reached to its critical point (31.1 °C and 1072 Psi), the temperature was kept constant at around 40 °C while the pressure was maintained at 1200 Psi. The samples were left in the supercritical CO₂ for 2 hours. After 2 hours, the vent valve was opened slowly (around 3-4 hours venting time) to vent the gas inside the chamber, and the samples were removed from the chamber.

Figure 3.2 shows the phase diagram of CO₂. In this phase diagram, A indicates the point where the chamber is filled with liquid CO₂ (around 18 °C and 955 Psi). After heating the chamber, CO₂ passes the critical point and reached to the point B (40 °C and 1200 Psi). Finally, CO₂ is vented while the temperature is constant at 40 °C, and the drying process is complete (point C).

**Figure 3.2:** Pressure - temperature phase diagram of CO₂.
3.2. Laser Exposures and Raman Scattering Measurements

Raman scattering, a spectroscopic method based on inelastic scattering of photons, was first observed by C. V. Raman in 1928. Since Raman spectrum of a substance provides characteristic information about the molecular and crystal structure, Raman scattering has been widely used for identification of molecules and materials [29].

When light interacts with matter, photons can either pass through without interacting with the material or can be scattered or absorbed [30]. Most of the scattered photons experience no change in energy (i.e., elastic scattering) that is known as Rayleigh scattering. However, in the Raman scattering, the incident light is scattered inelastically, where the scattered photon loses or gains energy to/from a vibrational mode; i.e., phonon. As illustrated in Fig. 3.3, in light scattering, the incident light first excites an electron from a ground state to a virtual state. If the electron subsequently turns back to the same ground state, a photon is emitted having the same energy as the incident photon. This event is the Rayleigh scattering. However, the excited electron may relax to a vibronic state, which represents the coupling of the ground state with a vibrational mode, as seen in Fig. 3.3. In this case, the emitted photon has less energy than the incident photon by the energy of the vibrational mode. In the language of quantum mechanics, a phonon is created. This type of Raman scattering is called Stokes Raman scattering. On the other hand, as illustrated in Fig. 3.3, the electron may also be excited from a vibronic state and relax to the ground state. In this case, the emitted photon has higher energy than the incident one by an amount equal to that of the phonon. Equivalently, a phonon is annihilated transferring its energy to the photon. This event is called anti-Stokes Raman scattering [31].
In the present study, a Renishaw RM 1000 micro Raman system equipped with a CCD camera and Leica DMLM microscope was used for conducting and monitoring of the phase transformation. Raman scattering acquisitions were performed by an 1800 lines/mm grating. A Spectra-Physics 160-series Ar$^+$ laser of 514 nm was used as the excitation source. The system was calibrated with a (111) silicon wafer with reference to the 1$^{\text{st}}$ order Raman scattering peak of Si at 520.5 cm$^{-1}$.

For Raman scattering scans of vanadium aerogels, samples were placed on a microscope slide and all measurements were performed at room temperature in the dark. A 20× objective lens with numerical aperture of 0.4 was manually focused on the samples. The laser beam was defocused by 20% to disperse the irradiation over an area of 16.2 µm diameter.

First, the Raman spectrum of a vanadia aerogel sample was collected under 0.6 mW incident laser power at an accumulation of 200 seconds. Subsequently, the incident laser power was increased to 6mW at which the transformation of the material occurs, and a new spectrum was collected under the same conditions. After transformation,
during which the second spectrum was collected, the power was decreased to its initial value (0.6 mW), and another Raman scan performed and recorded.

3.3. Temperature Measurement by Raman Spectroscopy

Besides molecular or materials identification, Raman scattering may also be used as a sensitive tool for temperature measurement [6, 7]. For a given vibrational mode, the ratio of anti-Stokes Raman scattering intensity to Stokes Raman scattering intensity is a Boltzmann factor, from which the temperature can be derived. This relation is given by

\[
\frac{I_{as}}{I_s} = e^{-E_p/kT}
\]

which is essentially the Boltzmann distribution function, where,

- \( I_{as} \) = Intensity of the anti-Stokes line
- \( I_s \) = Intensity of the Stokes line
- \( E_p \) = Phonon energy (i.e., Raman shift)
- \( k \) = Boltzmann constant \((1.38 \times 10^{-23} \text{ J/K})\)
- \( T \) = Temperature (K)

Here the photon energy \( E_p \) was calculated by using the relation:

\[
E_p = \frac{hc}{\lambda}
\]
where,

\[ hc = 1.24 \text{ eV} \times \mu \text{m} \] (h is the Planck's constant and c is the speed of light),

\[ \frac{1}{\lambda} = \text{wavenumber of the Raman peak}. \]

In the present study, the temperature at which the \( V_3O_7\cdotH_2O \) to \( V_2O_5 \) phase transformation of vanadium aerogels occurs was measured by Raman scattering. Since the \( V_3O_7\cdotH_2O \) anti-Stokes peaks yield poor signal to noise ratio, \( V_3O_7\cdotH_2O \) was first partially transformed to \( V_2O_5 \) at around the transformation threshold laser intensity. Typically, the transformation was driven to \(~33\%\) completion. At around the threshold laser intensity, the transformation can be slowed down and a mixed phase can be obtained controllably. Then, the temperature measurement was based upon Stokes and anti-Stokes peaks of the \( V_2O_5 \) phase, which yields significantly sharper Raman peaks at higher signal to noise, as will be disclosed in Chapter 4. Once the transformation is significantly slow, \( V_2O_5 \) phase is in thermal equilibrium with the \( V_3O_7\cdotH_2O \) phase. Therefore, the temperature calculation was based on Stokes and anti-Stokes peaks of the \( V_2O_5 \) phase.

In order to find the lowest laser power (i.e., threshold) at which the phase transformation occurs, and the two phases coexist, the laser beam was focused on the samples by a 20× objective lens where the laser spot size on the sample was adjusted to 33.3 \( \mu \text{m} \). Raman scattering was performed under different laser powers, until the lowest incident power level, at which the Raman peaks associated with \( V_2O_5 \) appear in the spectrum. This power threshold was found to be 2.66 mW. Thus, temperature measurement was performed by collecting Stokes and anti-Stokes peaks separately with
the 20× objective lens under 2 mW incident power at an accumulation of 200 seconds. Intensities of the Stokes peaks at 405 and 283 cm\(^{-1}\) and the anti-Stokes peaks at -405 and -283 cm\(^{-1}\) for V\(_2\)O\(_5\) were used for the calculation of transformation temperature.

**3.4. Raman Acquisitions in Argon Ambient**

In order to investigate the V\(_3\)O\(_7\)·H\(_2\)O to V\(_2\)O\(_5\) transformation in an inert environment (e.g., oxygen-free and water-free), samples were enclosed in septum-sealed optical cells, which were subsequently purged with argon gas. Two syringe needles were pierced into the septum; one for gas intake which was connected to the argon cylinder, and the other for gas exit which was open to the atmosphere. Argon pressure was kept at around 1 psi to allow a laminar flow without harming the sample, while the original air inside the cell was purged off through the other needle. Samples were purged for at least 10 minutes. At the end of the purging, the needle open to the atmosphere was removed first.

The Raman scattering of the sample kept in argon was performed with 20× objective lens (numerical aperture of 0.4). The laser beam was defocused by 20% to disperse the irradiation over an area of 16.2 μm diameter.

**3.5. Electronic Band Gap Calculation**

To the best of the author’s literature search, no information is available on the electronic and optical properties of V\(_3\)O\(_7\)·H\(_2\)O. Accordingly, optical absorption scans were carried out to estimate the electronic band gap of V\(_3\)O\(_7\)·H\(_2\)O. Since, the sol-gel synthesized vanadia samples are opaque and they cannot be cleaved to thin films due
their extreme fragileness, measurements were performed with samples dissolved in deionized water at a concentration of 3.4 g/l. Cary 300, a double beam spectrophotometer was employed to measure the optical transmission using deionized water as the reference. Both the water reference and the vanadia sample were enclosed in Starna UV-Vis optical cells. The transmission coefficient (T) was converted to absorbance (A) as

\[ A = -\log (T) \]  

From which the band gap was derived as will be discussed in Chapter 4.

3.6. Transformation Kinetics by Photoluminescence

The V$_3$O$_7$.H$_2$O to V$_2$O$_5$ transformation kinetics was monitored from the intensity of V$_2$O$_5$ photoluminescence (PL) in time series, where V$_3$O$_7$.H$_2$O essentially exhibits no PL, while V$_2$O$_5$ has a broad emission under 514.5 nm excitation. Renishaw RM 1000 micro Raman system was employed for the PL acquisitions. All PL measurements were performed by a 150 lines/mm grating using a 20× objective lens (0.4 numerical aperture) in time series, acquiring a spectrum at every 2 seconds (1 second excitation time), for a total of 100 seconds at 0.8 mW incident laser power. The laser irradiation was dispersed over an area of 16.2 µm diameter by defocusing the laser beam by 20%. 

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CHAPTER 4
RESULTS AND DISCUSSION

4.1. Physical Characterization of Samples

Vanadium aerogels were prepared as described in Sections 3.1.2 and 3.1.3. During the preparation process the water/acetone solution, vanadium (V) tripropoxide and precursor solution were cooled in order to prevent quick gelation. The obtained samples were dried by supercritical drying with liquid CO$_2$ as described in Section 3.2. Supercritical drying of aerogels allows slow extraction of acetone from gels and prevents the collapse of the structure due to the capillary forces. The synthesized wet-gels had a reddish color before the aging process. During the aging, the color of aerogels changed to brown and finally to dark green (Fig. 4.1).

Structure of the vanadia aerogels was studied by a FEI Quanta 600 field-emission scanning electron microscope (SEM). SEM image in Figure 4.2 shows that the structure of vanadia aerogels consists of 15 to 20 nm diameter, and microns long nanowire building blocks.
**Figure 4.1:** Sol-gel synthesized $\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$.

**Figure 4.2:** SEM image of sol-gel synthesized $\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$.
Aerogel samples were also characterized using PanAnalytical XPert X-ray Powder diffractometer with a Pixel detector using Cu K$_a$ (0.152 nm) radiation. Figure 4.3. shows the X-ray diffraction (XRD) spectrum of a typical aerogel sample. The diffraction peaks reveal a nanocrystalline material. The optimal fit for the observed X-ray spectrum was found to be orthorhombic $\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$ (trivanadium pentaoxide hydrate) [34]. In addition, the XRD spectrum as well as its assignment are in agreement with the previous work of Leventis et al. [27]. Further, their XPS findings revealed that the vanadium is present as vanadium(V) and vanadium(IV) at fractions of 67.61% and 32.39%, respectively.

**Figure 4.3:** XRD spectrum of a vanadium oxide aerogel sample. The line spectrum represents $\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$ for comparison (JCPDS-85-2401).
Finally, vanadia aerogels were characterized by Raman scattering as described in Section 3.2. Figure 4.4.a shows the Raman spectrum of a typical vanadia aerogel.

### 4.2. Laser Induced Phase Transformation of Vanadia Aerogels at 514 nm

During the Raman scattering acquisitions, we discovered a phase transformation of the V$_3$O$_7$.H$_2$O aerogel to V$_2$O$_5$ under 514nm laser above a certain threshold laser intensity. The phase transformation was clearly monitored from the dynamic Raman spectrum of the sample under excitation.

Figure 4.4.a shows the Raman spectrum of vanadia aerogels before the transformation at 0.29 kW/cm$^2$ incident laser intensity. On the other hand, Figure 4.4.b is the Raman spectrum collected with ten times the laser intensity; i.e., 2.9 kW/cm$^2$. Obviously, the higher laser intensity spectrum is different indicative of a phase transformation or chemical reaction. The captured Raman spectrum during this transformation is dominantly characteristic of V$_2$O$_5$. After the material is fully transformed, a final Raman spectrum of the aerogel was collected at 0.29 kW/cm$^2$ incident laser intensity that is provided in Fig. 4.4.c. As can be seen in Fig. 4.4, there is also a reduction in the background of the Raman spectrum. In view of Raman scattering literature, this new phase is identified as crystalline V$_2$O$_5$ [35].

The assignments of Raman peaks in spectrum of V$_2$O$_5$ are as follows. The mode at 995 cm$^{-1}$ is V═O stretching. The 703 cm$^{-1}$ peak corresponds to V─O stretching of doubly coordinated oxygen (associated with the corner shared oxygens). The 527 cm$^{-1}$ mode is the V─O stretching from triply coordinated oxygen (associated with the edge-shared oxygen). The mode at 483 cm$^{-1}$ is the bending vibration in V─O─V groups. The
405 and 283 cm\(^{-1}\) peaks are due to the V=O bending, and finally, 196 and 145 cm\(^{-1}\) are the lattice vibrations due to the layered structure of V\(_2\)O\(_5\) [36, 37].

**Figure 4.4:** Raman spectra of vanadia aerogel sample: a) V\(_3\)O\(_7\)·H\(_2\)O before laser exposure at 0.29 kW/cm\(^2\) intensity; b) vanadia, which was originally V\(_3\)O\(_7\)·H\(_2\)O but immediately transformed to V\(_2\)O\(_5\) during Raman scan (200 s) at 2.9 kW/cm\(^2\) laser
intensity c) transformed material (V₂O₅) after laser exposure as in (b) However, 0.29 kW/cm² laser intensity was employed for the Raman acquisition.

As seen in the optical micrograph of Fig. 4.5, a distinct color change was observed at the spot, which was exposed to the laser. This color change is attributed to the phase transformation to V₂O₅. Further, during the transformation, the scattered laser radiation from the spot (after attenuation by a factor of 100) was captured in a video. Typically, the image of the scattered laser from the sample surface is observed as an interference pattern with an ensemble of bright spots. Interestingly, random blinking of these spots was observed during the course of the transformation indicative of structural changes on the surface. Eventually, this blinking ended implying the completion of the transformation. The laser transformed region was also examined by SEM as shown in Fig.4.6. It is observed that the transformed V₂O₅ region has undergone a volumetric contraction and increase in density of vanadia wires.

![Figure 4.5: Optical image showing laser exposed region of a typical vanadia aerogel.](image)
Figure 4.6: Scanning electron microscope image showing the laser exposed region of the vanadia aerogel which is in the lower half of the picture and bordered by the crack.

It has been observed that the same phase transformation occurs in an inert environment. As described in Section 3.4., the transformation in an inert environment was investigated by placing the vanadia aerogel in an optical cell purged with argon. First, the sample was transformed at 6 mW incident power. Subsequently, incident power was decreased to 0.6 mW, and Raman scan was performed and recorded for an accumulation of 200 seconds. As seen in Fig. 4.7, a similar spectrum was observed with an additional peak of 879 cm$^{-1}$. 

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Figure 4.7: Raman spectrum of vanadia aerogel transformed to V$_2$O$_5$ in Ar environment.

At first, we associated the 879 cm$^{-1}$ peak with the presence of the inert environment. In particular, we suspected this peak to be a marker of defect creation due to the absence of oxygen in the medium. Since, V$_2$O$_5$ contains higher amount of O covalently bonded to V, one expects the transformation consumes O from its environment. Accordingly, the absence of oxygen may prevent establishment of certain V–O bonds leading to the creation of defects. However, later it was observed that the 879 cm$^{-1}$ peak was also observed in air environment when the sample is transformed at low laser irradiation, i.e., around threshold, as the transformation proceeds slowly. However, this peak was observed to be unstable and disappear while the transformation was in progresses. This Raman peak at 879 cm$^{-1}$ is found to identify the presence of H$_2$O$_2$ [38]. In particular, it is assigned to O–O stretching in H$_2$O$_2$ [38]. Accordingly, the 879 cm$^{-1}$ Raman peak suggests that H$_2$O$_2$ is produced as a by-product during the transformation.
The disappearance of the 879 cm\(^{-1}\) peak is simply attributed to the instability of H\(_2\)O\(_2\), which breaks down to H\(_2\)O and O\(_2\).

An interesting feature of the V\(_3\)O\(_7\)-H\(_2\)O to V\(_2\)O\(_5\) transformation investigated here is its occurrence at a remarkably low laser intensity (e.g., 0.31 kW/cm\(^2\)). This low laser intensity immediately suggests negligible heating effects suggesting the transformation is completely driven optically. In other words, the transformation is expected to be of athermal origin. However, to confirm the athermal nature of the transformation, in situ determination of the temperature during transformation was needed.

As detailed in Section 3.3., this temperature determination was accomplished by Raman spectroscopy. Figure 4.8 shows Stokes and anti-Stokes Raman peaks of vanadia aerogels at laser irradiation close to the threshold for transformation. Raman peaks at ±405 and ±283 cm\(^{-1}\) were used for the calculations which are well defined peaks associated with the V\(_2\)O\(_5\) phase. The temperature during the transformation was found to be in the range of 25-29 °C.

Although our measurements suggest that the impetus for the V\(_3\)O\(_7\)-H\(_2\)O \(\rightarrow\) V\(_2\)O\(_5\) transformation is athermal under 514 nm laser radiation, for a rigorous conclusion we also explored thermal conversion of V\(_3\)O\(_7\)-H\(_2\)O to V\(_2\)O\(_5\) by furnace annealing. When the samples were annealed in the furnace, the V\(_3\)O\(_7\)-H\(_2\)O \(\rightarrow\) V\(_2\)O\(_5\) transformation was observed to take place at around 350 °C. A color change from dark green to yellow was observed indicative of a phase transformation. Figure 4.9 shows the Raman spectrum of the sample after annealing at 350 °C confirming the presence of V\(_2\)O\(_5\) and thereby the V\(_3\)O\(_7\)-H\(_2\)O \(\rightarrow\) V\(_2\)O\(_5\) transformation. In conclusion, this experiment has proven the
The athermal nature of the $V_3O_7\cdot H_2O \rightarrow V_2O_5$ transformation under 514 nm laser, because the measured temperatures during the transformation separately for laser exposure and furnace annealing cases show a dramatic departure; i.e., 25-29 °C vs. 350 °C.

Interestingly, the same $V_3O_7\cdot H_2O \rightarrow V_2O_5$ transformation was observed by Zakharova et al. in $V_3O_7\cdot H_2O$ nanobelt samples annealed at 400 °C [9]. They suggest that the similarity in crystal structures of the two phases (i.e. $V_3O_7\cdot H_2O$ and $V_2O_5$) facilitate the transformation, so that it can occur at 400 °C. They also explain the transformation as a simultaneous dehydration and oxidation of $V_3O_7\cdot H_2O$ upon heating that can be expressed in the following equations;

\[
V_3O_7 \cdot H_2O \rightarrow V_3O_7 + H_2O \tag{4}
\]

\[
4V_3O_7 + O_2 \rightarrow 6V_2O_5 \tag{5}
\]

In the light-induced transformation investigated by the present thesis, $H_2O_2$ is likely to be released with $H_2O$. Alternatively, $V_3O_7\cdot H_2O$ may play a catalytic role in transforming $H_2O$ partially to $H_2O_2$. It is unclear how $H_2O_2$ is produced and how it impacts the transformation. However, it is likely that the $O_2$ released from the dissociation of $H_2O_2$ may facilitate the reaction given by Equation 5 above.
Figure 4.8: a) Anti-Stokes Raman spectrum of semi-transformed vanadia aerogel; b) Stokes Raman spectrum of semi-transformed vanadia aerogel.

Figure 4.9: Raman spectrum of the aerogel sample after annealing at 350 °C
4.3. Transformation Kinetics by Photoluminescence

As mentioned in Section 3.6, the kinetics of $\text{V}_3\text{O}_7\text{H}_2\text{O}$ to $\text{V}_2\text{O}_5$ transformation under laser irradiation was monitored by photoluminescence. Here, one may question why PL was used instead of Raman scattering. Although, high signal to noise Raman spectra of $\text{V}_2\text{O}_5$ is obtainable, such a scan at around the threshold laser intensity requires tens of seconds for an acceptable signal to noise. This situation is valid especially at the beginning of the transformation, when the $\text{V}_2\text{O}_5$ phase is minor. However, a time resolution of tens of seconds, can not resolve the transformation, which takes about 100 s. This problem cannot be addressed by increasing the laser intensity that increases the transformation rate requiring shorter integration times. Fortunately, the PL of $\text{V}_2\text{O}_5$ provides reasonable signal to noise at around the threshold intensity at an integration of 2 s, even at the beginning of the transformation.

Figure 4.10 shows the time evolution PL spectra for a vanadia aerogel sample as it transforms to $\text{V}_2\text{O}_5$ at 0 s, 10 s, 20 s, 30 s, 40 s, 60 s, and 100 s. Each spectrum was integrated for 2 s. The time series PL intensity (maximum) in intervals of 2 s is given in Fig. 4.11. The solid line in the plot represents a theoretical fit of the form.

$$I = I_{\text{max}} (1 - e^{-at}) \tag{6}$$

where,

$I = \text{PL intensity at time } t,$

$I_{\text{max}} = \text{Saturation PL intensity},$

$a = \text{Rate constant}.$
Figure 4.10: PL spectra for vanadium oxide aerogel as it transforms to $V_2O_5$ captured at 0 s, 10 s, 20 s, 30 s, 40 s, 60 s, and 100 s.

Figure 4.11: Kinetics of $V_3O_7 \cdot H_2O \rightarrow V_2O_5$ transformation as monitored by PL. Inset shows transformation rate constant as a function of laser intensity.
The relation in Equation 6 is not consistent with nucleation and growth in 2D or 3D. Basically, nucleation and growth occur either by instantaneous nucleation from predetermined nucleation sites, or progressive nucleation where nucleation and growth occur simultaneously [39]. However, in both regimes the initial kinetics should show a superlinear trend due to the increase in the interface between the transformed and untransformed regions. Accordingly, these mechanisms are expected to yield an “S-shaped” kinetics curve that is not observed in the present case. Therefore, two alternative growth models are proposed. An alternative model is that, nucleation occurs at predetermined sites and growth proceeds in 1D. In 1D growth and without progressive nucleation, the interface between the two phases does not increase by time. Rather, the coalescence of the transformed regions eventually decreases the interface area, as the transformation proceeds. This mechanism is consistent with $V_3O_7\cdot H_2O$ nanowires, which essentially behave as 1D structural elements. The transformation front in nanowires should move in 1D along the length of the nanowires.

According to the second model, nucleation is not rate limiting and phase transformation occurs as a simple chemical reaction. Equation 6 equivalently argues that the $V_3O_7\cdot H_2O$ phase is subject to exponential decay in time: $m(t) = m_o e^{-at}$, where $m_o$ is the initial untransformed mass of $V_3O_7\cdot H_2O$ and $m(t)$ is the remaining mass after a transformation time of $t$. $a$ is the transformation rate constant as defined above. As an example, exponential decay is commonly observed in photobleaching of dye molecules [40]. The justification for this mechanism could be the removal of an activation barrier for the transformation from $V_3O_7\cdot H_2O$ to $V_2O_5$ under laser excitation due to the proximity
between the structures of the two phases. The athermal nature of the transformation is in accord with this explanation.

The inset in Figure 4.11 shows transformation rate constant, \(a\), as a function of laser intensity. \(a\) was derived from the least square fit of kinetics data as in Figure 4.11 to Equation 6 for various laser intensities. Further, \(a\) was fit to an exponential relation of the form \(a = Ae^{b(I-I_t)}\) where \(A\) and \(b\) are fitting constants (\(A=1.28\times10^{-4}\) and \(b=5.69\) cm\(^2\)/kW), \(I\) is the laser intensity, and \(I_t\) is the threshold laser intensity (0.63 mW).

4.4. Band gap of V\(_3\)O\(_7\)-H\(_2\)O

Optical absorbance of V\(_3\)O\(_7\)-H\(_2\)O is shown in Fig. 4.12 for a nanowire concentration of 3.4 g/L in water, from which the band gap was deduced as 1.97 eV. The absorbance is seen to have two regimes: 1) a superlinear regime above a threshold of \(\cong 2\) eV which is reminiscent of band to band absorption in a semiconductor; 2) a linear regime below \(\cong 2\) eV which is either attributable to subgap absorption due to defects, or a residual phase, or light scattering. Accordingly, the absorbance, \(A(E)\), can be fit into the form:

\[ A(E) = L(E) + C(E - E_g)^n, \]

where \(E\) is the photon energy and \(L(E)\) is the linear component. For a semiconductor, optical absorption due to transitions from valence to conduction band is of the form \(C(E - E_g)^n\), where \(E_g\) is the band gap, and \(C\) and \(n\) are appropriate constants. As discussed above, \(L(E)\) may be fit into a linear relation to a first approximation. In the inset of Fig. 4.12, a semilog plot of \(A(E) - L(E)\) is provided which expected to yield an asymptote at \(E_g\), if it obeys a relation of the form \(C(E - E_g)^n\).
Clearly, an asymptote is observed at 1.97 eV which is the predicted value for the band gap. Once, L(E) is approximated as linear, E_g may also be clearly predicted from the 1\textsuperscript{st} and 2\textsuperscript{nd} derivatives of A(E). Conducting this analysis E_g is again found to be 1.97 eV. Although, calculation of the band gap involves some approximation here, it is accurate enough to show that V_3O_7·H_2O has a lower band gap than V_2O_5 by \( \pm 0.5 \) eV.

**Figure 4.12:** Optical absorbance of V_3O_7·H_2O. Inset shows the semilog plot of A(E) – L(E) (where A(E) is the absorbance, and L(E) is the linear part of the absorbance).
CHAPTER 5

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The following conclusions are drawn from the results of the present thesis work.

The author also has suggestions for the advancement of the findings presented so far.

1) A light-induced phase transformation of $V_3O_7\cdot H_2O$ to $V_2O_5$ was discovered under 514 nm laser radiation at a remarkably low laser intensity (i.e. as low as 0.31 kW/cm$^2$).

2) The temperature during the $V_3O_7\cdot H_2O$ to $V_2O_5$ transformation was found to be in the range of 25-29 °C that confirms the athermal origin of the transformation.

3) It was observed that the same $V_3O_7\cdot H_2O$ to $V_2O_5$ transformation occurs at 350 °C when driven thermally without laser radiation.

4) The light-induced transformation of $V_3O_7\cdot H_2O$ to $V_2O_5$ was observed to persist in argon environment under the same conditions suggesting that the transformation can proceed without the presence of oxygen in the surroundings.
5) The appearance and subsequent disappearance of the 879 cm\(^{-1}\) Raman peak implies that H\(_2\)O\(_2\) is produced as a by-product during the transformation.

6) The transformation kinetics, which fits into the relation \( I = I_{\text{max}}(1 - e^{-at}) \), may be explained by two alternative models: a) nucleation occurs at predetermined sites and growth proceeds in 1D. This mechanism is consistent with V\(_3\)O\(_7\)-H\(_2\)O nanowires, which essentially behave as 1D structural elements; b) nucleation is not rate limiting and phase transformation occurs as an ordinary chemical reaction. The justification for this mechanism could be the removal of an activation barrier for the transformation from V\(_3\)O\(_7\)-H\(_2\)O to V\(_2\)O\(_5\) under laser excitation due to the proximity between the structures of the two phases. The athermal nature of the transformation is in accord with this explanation.

7) Future work must further elucidate the light-induced mechanism of the V\(_3\)O\(_7\)-H\(_2\)O to V\(_2\)O\(_5\) transformation. In light of Zakharova et al., this transformation is facilitated by the close crystal structures of the two phases that involves minimal conformational changes during the transformation. The impact of the light could be further facilitation of the transformation by elimination of the hydrogen bonds associated with water. The light-induced transformation could be a result of a photocatalytic interaction of VO\(_6\) or VO\(_5\) units with the water already inside the structure.

8) Therefore, termination of hydrogen bonds during the light-driven transformation as well as formation of free water must be investigated by Raman spectroscopy in higher wavenumber range (i.e., 2000-4000 cm\(^{-1}\)).
9) The dehydration process during the transformation as well as production of H$_2$O$_2$
could be due to the photocatalytic attribute of the V$_3$O$_7$·H$_2$O. It would be interesting and
elucidating to conduct a series of experiments, which involve immersion of V$_3$O$_7$·H$_2$O in
H$_2$O$_2$ in dark as well as in H$_2$O under laser radiation and monitoring for the
transformation and production of H$_2$O$_2$, respectively.
BIBLIOGRAPHY


[34] JCPDS No: 085-2401, Powder Diffraction File.


IT\AA

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Scope and Method of Study:
In the present work, light-induced phase transformation of a transition metal oxide has been observed and studied. This phase transformation occurs between two different oxides of vanadium, prepared by sol-gel chemistry, namely from V₃O₇·H₂O to V₂O₅ under low laser irradiation. Raman scattering was used to monitor the phase transformation and measure the temperature during the transformation. In addition, the kinetics of the phase transformation was probed by photoluminescence. Electron microscopy images and X-ray diffraction data are provided for the elucidation of nanostructure and crystal structure.

Findings and Conclusions:
The V₃O₇·H₂O to V₂O₅ phase transformation as observed from Raman scattering was found to be occur under laser irradiation as low as ≅0.31 kW/cm². An interesting feature of this phase transformation is found to be its athermal origin. In addition, the V₃O₇·H₂O to V₂O₅ transformation was observed to persist in argon environment under the same conditions suggesting that the transformation can proceed without the presence of oxygen in the surroundings. Raman spectroscopy was also employed to rule out the heating effects and measure the temperature during this transformation which is as low as 25-29 °C (i.e., measurements performed at room temperature). In contrast, it was observed that the same transformation occurs at 350 °C when it is driven thermally by annealing samples for 10 minutes. The kinetics of the transformation as measured from photoluminescence suggests 1D nucleation and growth from predetermined nucleation sites. The appearance and subsequent disappearance of the 879 cm⁻¹ Raman peak implies that H₂O₂ is produced as a by-product during the transformation.

ADVISER’S APPROVAL: Dr. A. Kaan Kalkan