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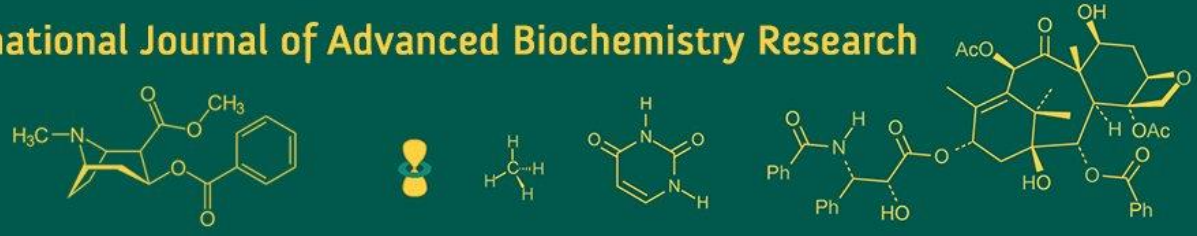

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Preparation, characterization of Nb-TiO_2 and its application in color degradation study

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Abstract
Color degradation over time. Absorption spectra changes at 663 nm and 274 nm. Formation of Niobium Titanate at high temp. Crystallite size (~126 Å). Lattice expansion due to Nb doping. High photocatalytic activity of Nb-TiO_2.

Keywords: Rutile, anatase, brookite, calcination, thermo gravimetric analysis (TG), differential scanning calorimetry (DSC)

Introduction

Medicinal plants have greatly gained importance in the management and treatment of human Titanium dioxide, known as titania, is a naturally occurring oxide of titanium. Its chemical formula is TiO_2 and molecular mass is 79.88. It occurs in three mineral forms namely rutile, anatase and brookite. TiO_2 is produced either in anatase or in rutile form. Most of the anatase is produced in white powder where as some of the rutile crystals are off white in color. Out of the forms of anatase and rutile, rutile is more stable and anatase to rutile transformation takes place at a temperature higher than 600^0. TiO_2 is most widely used in white pigment products such as paints, coatings, plastics etc. because of its brightness and high refractive index i.e. >2.4 which determines the opacity.

Titania absorbs light only in ultra violet region. But to make it more effective and usable in normal solar light doping in TiO_2 required. The selection of doping element depends on the oxygen affinity of that element. There can be many elements which can be used as dopant. In this particular project work, Nb is used as doping element. It introduces a new level of electronic state into the band structure of the parent material. Nb could form a solid solution in the crystal structure of TiO_2 due to the fact the size of Nb^{5+} ($0.64A^0$) is similar to that of Ti^{4+} ($0.605A^0$), thus the particle size in the doping samples were not affected by Nb atoms. Nb 4d orbital is strongly hybridized to TiO_2 3d orbital to form a d nature conduction band without impurity state in the in gap region resulting in high carrier density exceeding 10^{-21} cm^{-3} and excellent optical transparency in visible region. Nb doping in TiO_2 enhances photo catalytic activity.

In 2000, D. Morris *et al* [1] studied the photoemission and STM of of the electronic structure of Nb-TiO_2. High resolution core and valence level photoemission spectra of Nb-TiO_2 ceramics have been measured. Nb doping produces a well-defined photoemission peak in the bulk band gap of rutile, whose intensity increases with increase in doping level. Core level spectroscopy and resonant photoemission demonstrate that at low doping level the extra electrons associated with Nb doping are localized mainly on Ti rather than Nb. So, the highly doped material is better formulated as $Ti(IV)_{1-2x}$ $Ti(III)_x$ $Nb(V)_x$ O_2. A comparison of present result with V doped TiO_2 revels a simple quantitative difference between the two systems, in V doped TiO_2 material electrons are trapped on the dopant atom rather than on host cation sites. In 2008, Taro Hitosugi [2] studied the properties of TiO_2 based transparent conducting oxides, which exhibit transparent conducting properties comparable to those of indium tin oxide (ITO), the most widely used TCO. Epitaxial thin film growth of anatase Ti_{1-x} Nb_x O_2 (TNO) with $0.03 < x < 0.06$ exhibit a resistivity of $2\text{-}3*10^{-4}$ Ωcm and internal transmittance of ~95% in the visible light region. Furthermore, polycrystalline films deposited by the pulsed laser deposition and sputtering methods showed a resistivity of $4.6*10^{-4}$ and $6*10^{-4}$ Ωcm, respectively, at room temperature. It has also been highlighted that characteristics

that are unique to TNO which distinguish it from ITO such as high refractive index, high transmittance in infrared and high stability in reducing atmosphere.

Yujing Liu [3] studied Nb-TiO2 in which crystalline Nb-TiO_2 nanoparticles were synthesized via solvothermal procedures using tertiary-butyl alcohol as a novel reaction medium and their assembly into mesoporous films was investigated. The solvothermal procedure enables the preparation of crystalline doped and undoped non agglomerated titania nano particles whose size can be controlled from 4-15 nm by changing the reaction temperature and time. Substitution doping with niobium ion drastically increases the electrical conductivity of the titania particles. In contrast to the titania particles prepared by solvothermal synthesis in benzyl alcohol, those of similar size and crystallinity synthesized in tertiary-butyl alcohol can easily be dispersed at high concentration. The Nb doped titania nanoparticles can be assembled into regular three dimensional mesoporous structures with a narrow pore size distribution and high surface area.

In 2012, Chandrakant Dighavkar *et al* [4] studied the gas pollutant detection by using doped titania thick films. Thick film of pure titania and various concentration (1 wt%, 3 wt%, 5 wt%, 7 wt% and 10 wt%) of Cr_2O_3 and Nb were prepared on the alumina substrates using a screen printing technique. The doped films were fired at a temperature of 800ºC for 2h in an air atmosphere. Various oxidising and reducing gases were tested for these metal oxide doped films. Among these NH_3 and H_2S gas sensing properties for these thick films were investigated for Cr_2O_3 and Nb doped TiO_2 respectively at different operating temperatures. Pure TiO_2 was found to be insensitive to these gases. At 250ºC, 5 wt% Cr_2O_3 doped films have shown significant sensitivity (88.23%) to NH_3 gas whereas 1 wt% Nb doped films have shown highest sensitivity (98.78%) to H_2S gas at 200 °C [5]

Flame spray pyrolysis has been successfully used for preparation of undoped and 1- 5% Nb-TiO_2, nano powders for application to acetone and ethanol gas sensing. The particle size of the doped TiO_2 and Nb doped TiO_2 were in the range of 10-20 nm. In this journal the sensing properties for acetone was studied at operating temperatures of 300-400 °C and for ethanol the operating temperature was 250-400 °C. It was observed that out of all samples 3 at% Nb was dispersed on TiO_2 sensing films. And this particular doping concentration showed a good response in both acetone and ethanol and it was observed that the best response occurred at a temperature of 350 °C and 400 °C. There are many work has been done to study the properties of TiO_2 and doped TiO_2 which we can read from the references [5-10].

Experimental Method

Sample preparation

Powders such as Titanium dioxide and niobium pentoxide were used are of analytical grade. Nb-TiO_2 in different mol% of Nb in it were prepared by solid state method. A typical preparation method is given below.

Nb doped in TiO_2 in different mole concentration is calculated as below:

$$(\eta\ Nb)/ (\eta\ Nb+ \eta\ TiO_2) *100 = x$$

Where, x is the mole concentration of Nb,

η is the ratio of weight of substance(W) to molecular mass(M) of the substance(W/M).

Example 1

Preparation of 1mol% of Nb_2O_5-TiO_2 considering the total mass of the sample to be 20 g.

$$(\eta\ Nb)/ (\eta\ Nb+ \eta\ TiO2) *100 = 1$$

$$=> 99\ \eta\ Nb = 1\ \eta TiO2$$

$$=> 99\ (W_n/M_n) = 1\ (W_t/M_t)$$

$$=> W_n = (20*265.81)/ (99*79.866)$$

$$=> W_n = 0.6723\ g$$

$$=>\text{Weight of } TiO_2 = 20-0.6723 = 19.3277g$$

These powders (TiO_2 and Nb_2O_5) are mixed in a mortar pestle and to it few drops of acetone was added and this mixture was mixed thoroughly for 3-4 hours. After that the sample was placed in air tight polythene.

Similarly, the other samples with concentration 0.01%, 0.03%, 0.06%, 0.5%, 1%, 2%, 4%, 10%, 30% were prepared using the same formula and same procedure.

Pellet making: From the TG/DSC data the temperature at which it has to be heated was fixed. Considering the same data pellets were prepared (using the procedure given below) from the powder sample for calcinations study.

To the powder samples 2% PVA (poly vinyl alcohol) was added. The powder was mixed thoroughly and was placed in the die. The rod was inserted inside an hollow cylindrical pipe, from the other side another rod was inserted and this set was placed on a hydraulic press. Then the pressure was applied (nearly 1500 ton). Due to this pressure and the binder present in the powder sample was formed as the small pellets.

Thermo gravimetric (TG) analysis: TG stands for thermo gravimetric analysis. This is the method in which changes in chemical and physical properties of a material can be measured as a function of increasing temperature and time. It can provide information about physical phenomena such as second order phase transition including vaporization, sublimation, absorption, adsorption etc. Similarly, it can also provide information about chemical phenomena like dissolving, decomposition and solid gas reactions.

TG is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain during these processes. Here, four samples i.e. 0.5%, 1%, 2% & 4% were given for TG analysis. Results are given under result and discussion part (vide infra).

Calcination study: Further Samples were heated using a 1700 °C horizontal tube furnace. A tube furnace is an electric heating device used to conduct syntheses and purifications of inorganic compounds and occasionally in organic synthesis.

Results and Discussion

Fig. 1 shows the photograph of the powders in mixed form, pellet after heating at 960 °C and 1400 ºC

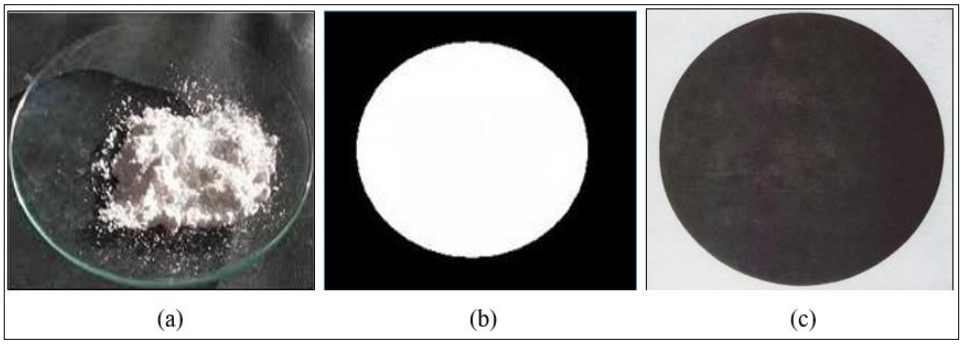


Fig 1: a. shows the powder sample with 1 drop of 2%PVA, b. shows the pellet formed after the application of 1500 ton pressure, c. shows the pellet after heating at 1400 °C for 4 h.

After heating the sample it is been seen that at 960 °C there is no change in the physical appearance of the pellet i.e. the color of the pellet remains colorless. But when the pellet is heated at 1400 °C for 4 hours it is clearly seen that there is a change in the color of the pellet. The color is due to the formation of a new compound of Nb-TiO_2 i.e. niobium titanate [11].

TG analysis

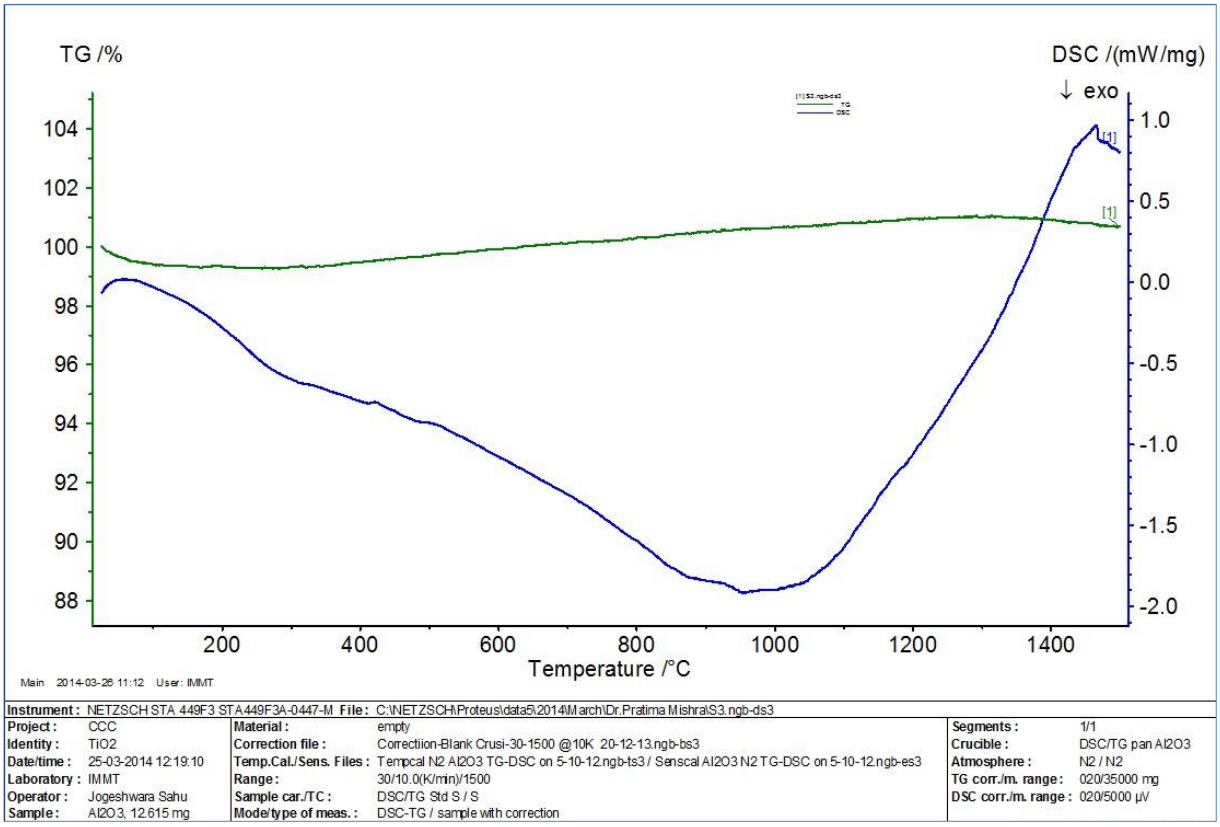
Table 1: Showing different samples having different phase change temperature

Sample	Temperature in °C
0.5% Nb-TiO_2	965.06
1% Nb-TiO_2	962.626
2% Nb-TiO_2	960.029
4% Nb-TiO_2	1041.653

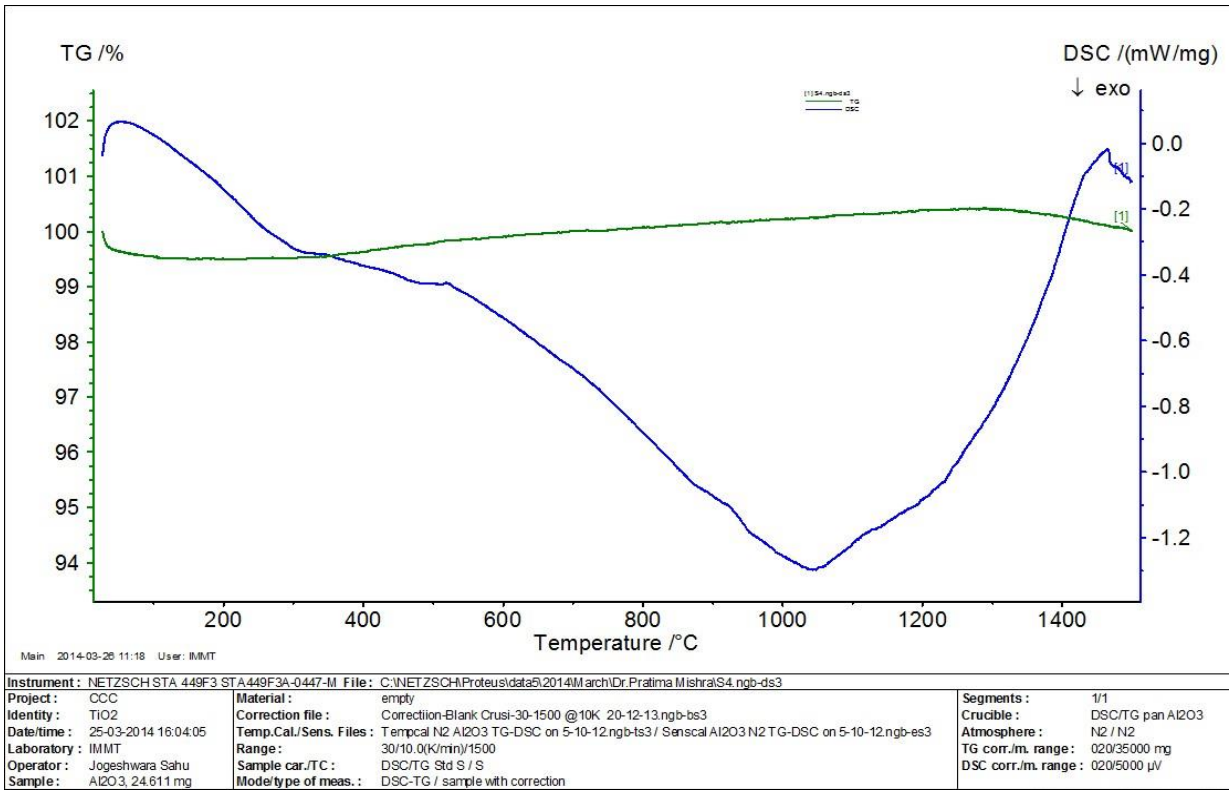
Figure 2 shows TG/DSC curve for a) 2% Nb-TiO_2 and (b) TG/DSC curve for 4% Nb-TiO_2

From the TG curve we observe that as the temperature increases there is a very negligible loss of mass and then it remains constant over total period of time. The mass loss may be due to some impurities, water vapor and acetone (used while mixing of powder sample).

Differential scanning calorimetry (DSC) curve shows that as the temperature increases there is a loss in the heat and after some time there is absorbance of heat (at a temperature of 962 °C in 2(a) and 1040 °C 2(b)). And after 1400 °C there is a change in phase.



(a)



(b)

Fig 2: (a) TG/DSC curve for 2% Nb-TiO2, (b) TG/DSC curve for 4% Nb-TiO2

Calcination study

The prepared powder sample and the pellet were heated to different temperatures i.e. 960 °C and 1400 °C in the tube furnace. The heating was done at temperature 960 °C there is a change in phase. So we have heated the pellets at 960 °C and at 1400 °C (to see the phase change).

The heating is done in different segments like

0-300 °C at 8 °C /min
Dwell time - 10 min
300-600 °C at 8 °C /min
Dwell time - 60 min
600-960 °C at 8 °C /min
Dwell time - 120 min
End

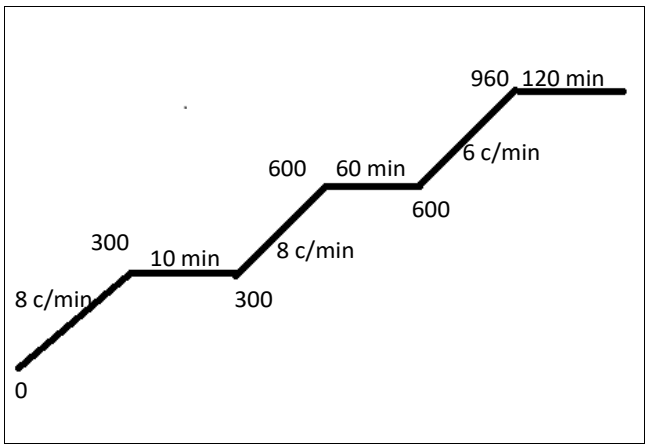


Fig 3: Steps showing the segments

At 600 °C we are keeping the dwell time of 60 minutes the binder i.e. 2% PVA evaporates and then we set the required temperature.

Phase, crystallite size analysis from XRD patterns

XRD data for heated Nb-TiO_2 samples as well as original TiO_2 powders were obtained. Fig 4 shows XRD data for TiO_2 showing peaks at (two theta values) 29.6115, 43.2929, 44.3112, 45.2098, 56.6723, 63.5930, 65.2020, 74.4124 which are due to anatase TiO_2 phase. Similarly, peaks were also observed for 0.06% Nb-TiO_2 [Fig 5] where peaks at 29.4778, 43.1678, 44.1772, 45.0918, 56.5494, 61.168, 63.6526, 64.4187 are obtained which is also in phase with anatase TiO_2. It was observed that all the samples show only one phase i.e. anatase.

Table 2 and Table 3 gives the peak values with corresponding 2ɵ value, full width half minima (FWHM) and the relative intensity data. From FWHM value we calculate the crystallite size (vide infra).

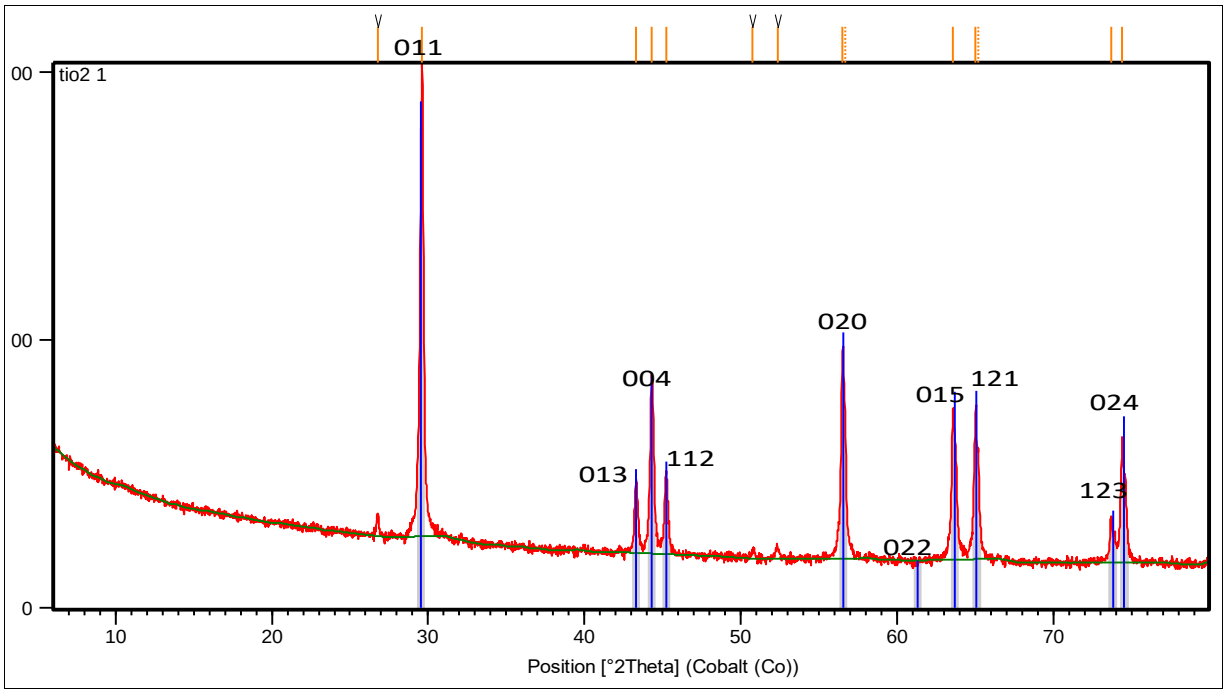


Fig 4: XRD data for TiO2 powder

Table 2: XRD Peak Positions (2θ)

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
26.7690	134.69	0.1338	3.86701	1.32
29.6115	10231.75	0.1506	3.50295	100.00
43.2929	495.25	0.1171	2.42669	4.84
44.3112	1792.97	0.1506	2.37364	17.52
45.2098	520.70	0.1004	2.32886	5.09
50.7752	24.41	0.4015	2.08787	0.24
52.3545	42.61	0.2007	2.02914	0.42
56.5206	2235.84	0.1428	1.88922	21.85
56.6723	1258.57	0.0816	1.88868	12.30
63.5930	1313.95	0.1428	1.69766	12.84
65.0383	1253.21	0.1836	1.66394	12.25
65.2020	747.39	0.0816	1.66384	7.30
73.6979	207.42	0.1632	1.49157	2.03
74.4124	945.14	0.1428	1.47929	9.24

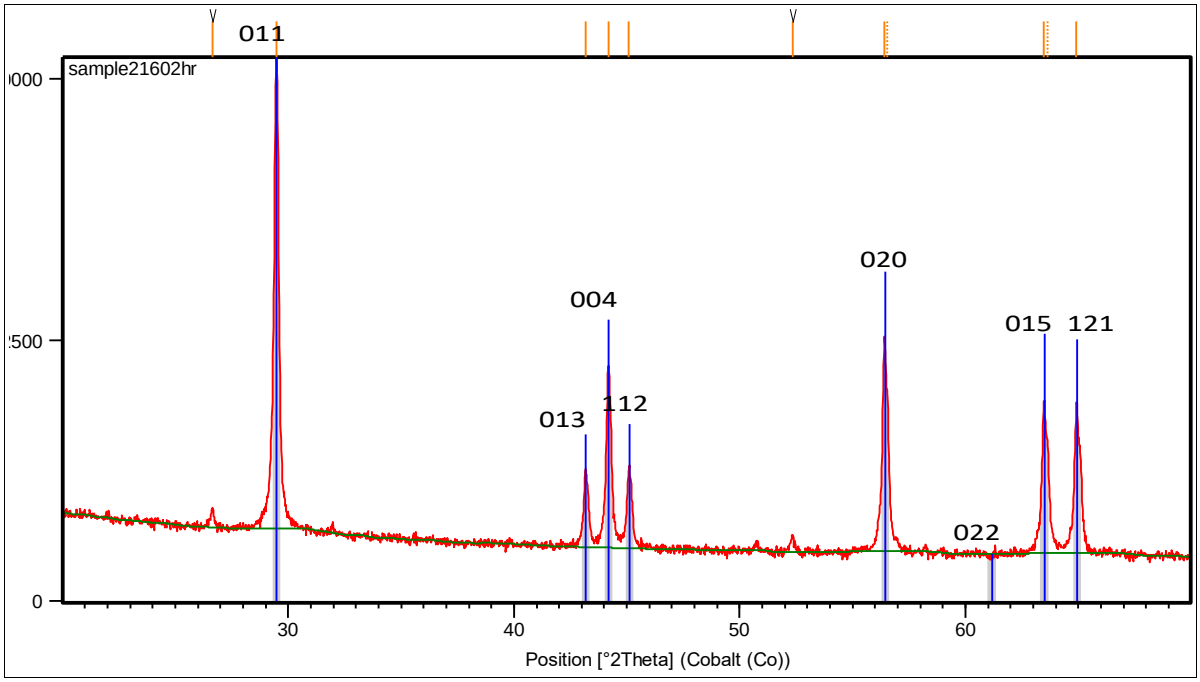


Fig 5: XRD data for 0.06% Nb-TiO_2

Table 3: FWHM Values Corresponding to XRD Peaks

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
26.6405	117.09	0.1338	3.88532	1.09
29.4778	10697.44	0.1506	3.51849	100.00
43.1678	545.96	0.0836	2.43339	5.10
44.1772	1900.14	0.1338	2.38048	17.76
45.0918	546.73	0.1004	2.33464	5.11
52.3359	58.97	0.2007	2.02981	0.55
56.4043	2370.36	0.1224	1.89280	22.16
56.5494	1409.61	0.0816	1.89245	13.18
63.4830	1391.39	0.1224	1.70030	13.01
63.6526	772.15	0.1020	1.69993	7.22
64.9187	1349.33	0.1020	1.66667	12.61

For other samples XRD patterns were taken but not shown here. In each case anatase grade titanium dioxide phases were obtained except for 30% Nb.TiO_2 sample. A comparative XRD patterns for three powders are shown here [Fig.6].

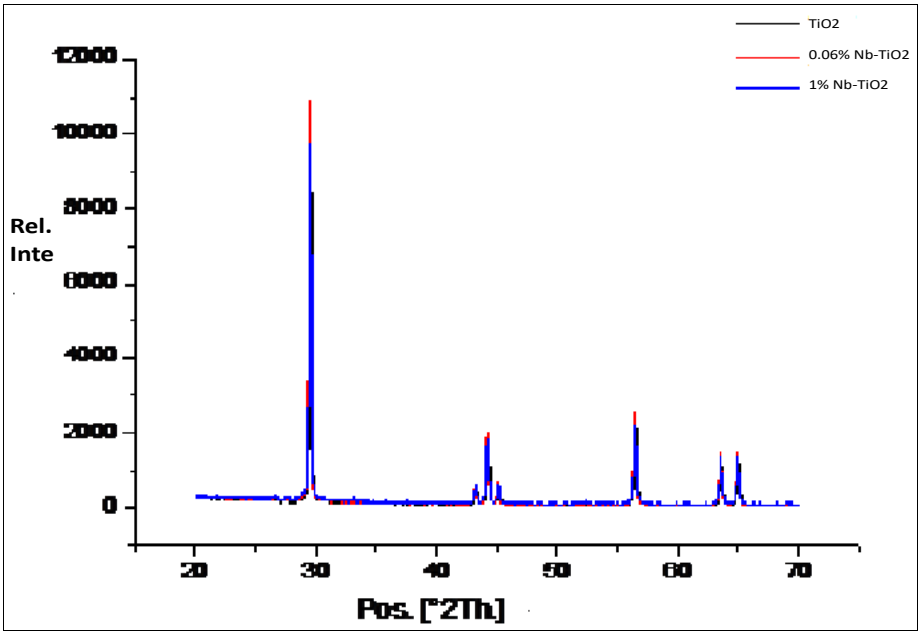


Fig 6: Comparison of phase of TiO_2, 0.06% Nb-TiO_2 & 1% Nb-TiO_2 samples

Calculation of lattice constants from XRD data

The d values were calculated using Bragg's law

$n\lambda = 2d \sin\theta$

Where, n is an integer, λ is the wavelength, d is the spacing between the planes in the atomic lattice, ɵ is the angle between the incident light and scattered plan

Since, TiO2 is tetragonal in shape, lattice constant can be calculated as

$$d = 1/(\frac{h2 + k2}{a2} + \frac{l2}{c2})$$

From this equation we can find the lattice constant using the relevant hkl values.

Where, hkl are the miller indices which can be found from the JCPDF file, a and c are the lattice constants. Since, the shape of TiO2 is tetragonal

Therefore, a=b=/=c

Ex:

hkl= 004

For this hkl value d= 2.37150 A^0

Using the formula we have

c=9.4860 A^0

Similarly, for hkl= 020

d=1.8880A^0

We found that a= 3.7760A^0

Table 4: To comparison of lattice constant values for different samples

Sample	hkl values	d in A^0	a, b & c in A^0
TiO_2	004 020	2.37364 1.88922	a= 3.77844 b= 3077844 c= 9.49456
0.06% Nb-TiO_2	004 020	2.38048 1.89157	a= 3.7849 b= 3.7849 c= 9.52192

It has been observed that both 'a' and 'c' values increase for doped samples showing a lattice expansion.

Determination of crystallite size

Similarly, crystallite size was calculated from the Scherrer equation (given below).

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

Where

τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size; K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite; λ is the X-ray wavelength; β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta(2\theta)$; θ is the Bragg angle.

Example

K=0.9

λ = 1.78 A= 0.178nm

2 Θ = 29.4778

Θ= 14.7389

FWHM = 0.1506 (2ɵ)

$\beta = \left(\frac{FWHM}{2}\right) * 0.017453$= (0.1506/2)*0.017453

=0.00131421 rad

cos Θ = 0.9670

Therefore, τ = (0.9*0.178)/(0.00131421*0.9670)

= 126.05824 A^0

Thus the crystal size was found to be 126.05824 A^0 A^0 for 0.06 mole% Nb- TiO2.

Similarly, for TiO2 and 1mole% Nb-TiO2 the crystal size were found and data are given in Table 5.

Table 5: Crystalline size for different samples

Sample	K	λ in nm	2ɵ	Θ	Θ*0.017453 in rad	Cosɵ	FWHM	B	*T* in nm
TiO2	0.9	0.178	29.6115	14.80575	0.258405	0.966799	0.1506	0.001314	126.0844
0.06% Nb-TiO_2	0.9	0.178	29.4778	14.7389	0.257238	0.967096	0.1506	0.001314	126.0456
1% Nb-TiO2	0.9	0.178	29.4959	14.74795	0.257396	0.967056	0.1506	0.001314	126.0508

It has been observed after Nb doping the crystallite size decreases. There is slight difference in size for both 0.06 and 1mol% Nb doping.

Color degradation of Methylene blue using Nb-TiO2 [12]

Nb-TiO_2 was taken for MB [made by FINAR reagents with catalog number 10951 and concentration 0.1%] color degradation study of methylene blue (MB).

The stock solution was made by adding 0.5ml of MB in 100ml water. Different bottles were taken and each bottle was filled with same amount of stock solution and to the stock solution 0.05 gm of Nb-TiO_2 was added.

The bottles were kept in the sunlight and after each 20 min, observations were taken.

The color of the stock solution gradually decreased and after 100 min the solution was totally colorless.

Figure 7 (a) shows the colored MB and figure 7 (b) shows how color of solution is degrading as time increases.

(a) (b)

Fig 7: This shows the color degradation property of Nb-TiO_2.

Absorption spectra

Absoption spectra of MB before and after the addition of the powder at different time [Fig 8]. It can be seen from the absorption graph that there are two main peaks at 663 nm and second at around 290 nm. The absorbation maxima was found to be 0.611567 at 663 nm. Absoption data with time at 663 nm is given in Table 5. It has been observed that MB absoption decreases with respect to time.

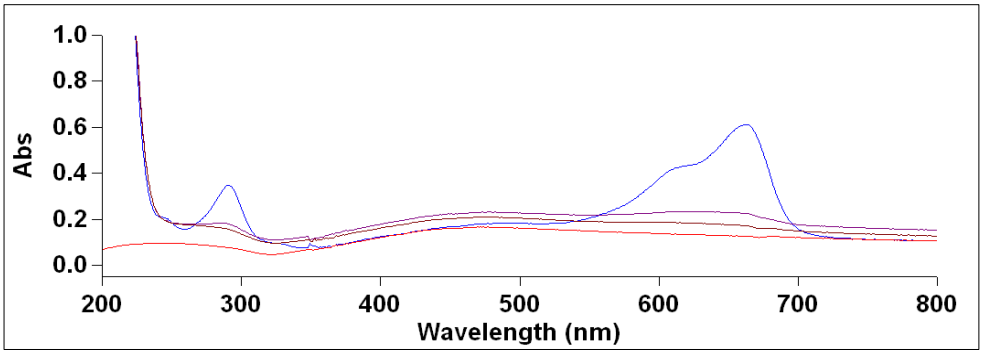


Fig 8: Graph shows wavelength vs absorption curve

Table 6: Absorption with wavelength

Wavelength in nm	MB	80 min	100 min
663	0.611567	0.223923	0.170716
274	0.214141	0.179226	0.169765

From table it can be seen that absorption value decreases as there is increase in time and if further time is taken than it would seen that absorption is totally zero.

In this report we have studies the properties of TiO2 and Nb-TiO2. From the XRD data it is clear that there is no change in the phase of Nb-TiO2.

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