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# Synthesis and Study the Structure, Morphological and Optical Properties Fortio$_2$-$Al_2O_3$-$La_2O_3$ Prepared by Chemical Bath Deposition

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**Abstract:- $TiO_2$-$Al_2O_3$-$La_2O_3$ thin films were prepared on glass substrates from solution of Ti [OCH(CH3)$_2$]$_4$, $AlCl_3.6H_2O$ and $LaCl_3.7H_2O$ at room temperature using a chemical bath deposition (CBD) method. The morphological, structural and optical properties of the $TiO_2$-$Al_2O_3$-$La_2O_3$ thin films were investigated using X-ray diffraction (XRD), field emission- scanning electron microscopy (FE-SEM), Fourier- infrared (FT-IR) spectrometer, Raman spectrometer and UV-VIS spectrophotometry. The XRD results showed that the average crystal size for $TiO_2$-$Al_2O_3$-$La_2O_3$ film at La concentration, with the hexagonal phase and the degree of crystallization strengthening after annealing. The Raman spectrum showed many small peaks and abroad peak, after annealed the intensity of peaks decreases with increasing the La concentration, and sharp peaks are observed in only at the first concentration and a large hump with increasing the concentration of (La). FT-IR spectra showed absorption peaks of different functional groups (i.e., O-H, C-O, Ti-O-Ti, Al-O and La-O), it's become sharp peaks after annealing with increasing concentration of La, which indicate of crystallization. FE-SEM images revealed 3D particles of $TiO_2$-$Al_2O_3$- $La_2O_3$ thin film, and the films were almost homogeneous and uniform. The bandgap energy (Eg) of $TiO_2$-$Al_2O_3$ doped with La thin film show decreased in the value with increase (La) concentration in both cases before and after annealing, respectively.**

***Keywords:-*** *$TiO_2$-$Al_2O_3$ -$La_2O_3$; CBD; Annealing; Morphological; Band-Gap Energy.*

## I. INTRODUCTION

The complex and tune able nature of the electrical properties of metal oxides makes them attractive and interesting materials for many applications such as solar cells, gas sensors, optoelectronics, photodetector, dental electronics, and photonic devices [1, 2]. The chemical and physical features of metal oxide nanoparticles are peculiar because they are small in size and have a high density of corner or edge surface sites [3]. Recently, many metal oxide nanostructures have been studied such as $TiO_2$, $Y_2O_3$, $La_2O_3$, $Gd_2O_3$, $Al_2O_3$, $HfO_2$, $ZrO_2$, $ZrSiO_4$, $HfSiO_4$ and $BaZrO_3$, ect. [4,5]. Titanium dioxide($TiO_2$) is a wide-gap n-type semiconductor that is highly transparent to visible light [6] chemical toughness and high refractive index in the visible and near Infrared region [7]. It is existing in three different phases anatase, rutile, and brookite. The active crystal phases of $TiO_2$ are anatase and rutile. [8,9]. there are many forms of $TiO_2$ such as nanowires, nano sheets, nano pillars, and nanotubes. It is the most widely used crystalline semiconductor in photo catalysis, because of it is relatively wide band gap energy (3.2, 3, 3.1) eV for anatase, rutilie, brookite respectively. The proprieties of $TiO_2$ are strongly depend on crystal structure, surface area, average particle size and porosity [10]. Due to its inexpensive nature, non-toxic, photoelectric properties, ability of photoelectric conversion, low-cost preparation and stabilization of the $TiO_2$ photocatalyst with small size particles is essential for practical applications [11-16]. Aluminum Oxide $Al_2O_3$ nanoparticles composite materials exhibit a particularly rich set of interesting physical properties, including conductivity, magnetic and optical [17]. It is having unique properties, such as low transmittance, high thermal conductivity, high dielectric constant, chemical and thermal stability [18], high refraction index [19], suitable hardness, and high radiation resistance, very good thermal and chemical stability [20,21], and high transparency [22]. $Al_2O_3$ offers a wide range of industrial applications such as anti-corrosion coating, anti-reflection coating, capacitive and humidity sensors, heat sinks ICs manufacturing various optoelectronic device such as (Silicon-Oxide-Nitride-Oxide-Silicon) semiconductor (SONOS), thin-film transistors (TFTs) and complementary metal-oxide-semiconductor (CMOS) devices, [23- 26].

$TiO_2$–$Al_2O_3$ nano-composite materials have many interesting physical properties, they protected metallic structural components from corrosion due to their thermal, mechanical and chemical stability [27,28], also improve the mechanical properties of materials such as bending strength, fracture toughness, hardness, resistance to wear, cavitation and oxidation [29,30], also used as refractory materials due to their excellent thermal expansion [31]. Recently, $TiO_2$–$Al_2O_3$ compounds have been very important for the fabrication of high-speed, high-quality passive electrochromic display in electronic applications [32]. lanthanum oxide ($La_2O_3$) has aroused great research interests due to its remarkable electrical, thermal, optical and chemical properties [33-35], $La_2O_3$ thin films can be found in several crystalline phases which are, cubic (c-$La_2O_3$) hexagonal (h-$La_2O_3$), amorphous (a-$La_2O_3$), or a mixture of the phases relying upon the

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technical of film deposition and post-statement heat treatment [36]. it has a band gap value of 4.3eV and presence as doped atom leads to narrower gap energy. [37]

On the other hand, has a high dielectric constant (≃27) it is one of the most promising high-k dielectric materials to replace $SiO_2$ and $Si_3N_4$ in an advanced metal-oxide gate stack in semiconductor devices [38]. It is commonly used as a kind of effective impregnation in heat emitters [39], oxide catalysts [40] and ferroelectric ceramics [41] in order to improve some properties such as effective dielectric constant, emittance, and catalytic activity. In addition, $La_2O_3$ thin films have also received increasing attentions for the various applications in gas sensor, super capacitor and glass ceramic [42-44], Therefore, in this study, of the crystallization and structure of $TiO_2$- $Al_2O_3$- $La_2O_3$ thin films is of great importance for the application compatibility of the films with all type of advanced devices electronic, optic and thermal. Therefore, in this study, we report the successful use of the simple versatile, economical and cost-effective chemical bath deposition (CBD) method to deposit a large area of $TiO_2$-$Al_2O_3$-$La_2O_3$ thin films and study the effect of annealing temperature on the structural, optical, and morphological characteristics of the prepared thin films.

## II. EXPERIMENTAL

### A. *Materials*

Titanium isopropoxide Ti $[OCH(CH_3)_2]_4$ (TTIP), (98%), purchased from Sigma-Aldrich Chemie, India was used as $TiO_2$ source. Aluminium chloride hexahydrate ($AlCl_3$. $6H_2O$), (97 %), from Merck, Germany was used as $Al_2O_3$ source, Lanthanum Chloride heptahydrate ($LaCl_3$.7($H_2O$), (99.99%), from BLD Pharmatech (India) was used as $La_2O_3$ source, Isopropanol ($CH_3CHOHCH_3$) (99 %) was obtained from Molychen. Mumbai, (India), and absolute ethanol ($C_2H_5OH$), (99.9%) from Changshu Hongsheng Fine Chemical Co Ltd., microscopic glass (dimensions 75 mm × 25 mm × 1.1 mm, used as a substrate. Before the deposition, the substrates were cleaned by using chromic acid, distilled water, acetone, ethanol, distilled water and finally allowed to air dry to remove the negligible amount of surface residues. All solvents and chemicals were of analytical grade and were used without further purification.

### B. *Deposition of $TiO_2$ - $Al_2O_3$ -$La_2O_3$ thin films*

The procedure for preparing of $TiO_2$-$Al_2O_3$- $La_2O_3$ thin films by CBD method consists of three main steps, including the solution preparation, formation of thin films and annealing the films.

- Step 1: Three solutions were prepared by dissolving (0.2M) TTIP in Ethanol $C_2H_5OH$ (40ml) and isopropanol (10 ml) to form a solution (A) and magnetically stirred at room temperature for 10 min for homogeneity.
- Step 2: three solutions were prepared by dissolving (0.05M) $AlCl_3$ .$6H_2O$ in Ethanol $C_2H_5OH$ (10ml) to form a solution (B) and magnetically stirred at room temperature for 2 h for homogeneity.
- Step 3: Three different concentration solutions were prepared by dissolving (0.01, 0.025, 0.05 M) $LaCl_3$.$7H_2O$ in Ethanol $C_2H_5OH$ (10ml) separately to form a solution (C) at three concentrations, and magnetically stirred at room temperature for 2 h for homogenization.
- Step 4: Solution (A) divide into 3 beakers and also solution (B) divide into 3 beakers.
- Step 5: Add first beaker from A to B and then to 0.01M of solution C, and same for 2nd and 3rd concentration. Then the last solution with 3 concentrations subjected to stirring for I h at 40º C and pH 4.
- Step 6: Two glass substrates were immersed into the resulting solution for 1 h at room temperature. The deposited films were then dried in air for 24 h, one of these prepared film was annealed at 500 ºC. $TiO_2$-$Al_2O_3$ -$La_2O_3$ nanostructures of High- quality and transparency were obtained Fig.1 and subjected to further characterizations.

### C. *Characterization techniques*

The deposited thin films were characterized for their morphological, structural, and compositional properties The crystal structure and crystallographic data were obtained from X-ray diffractometer (XRD) (Ultima IV of Rigaku Corporation, Japan) with Cu Kα (λ=1.54056 Å).

Fourier transform- infrared (FT-IR) spectra (FT-IR JASCO-4600) spectra were examined from 400- 4000 $cm^{-1}$ using the transmittance mode at room temperature.

Raman spectra were recorded on a Jobin Yvon Horibra LABRAM-HR instrument in the range of 50-5500 $cm^{-1}$ with a scanning resolution of 1 $cm^{-1}$, using back scattering geometry.

The surface morphology of the $TiO_2$-$Al_2O_3$- $La_2O_3$ films was examined by Field emission- scanning electron microscope (FE-SEM) using FESEM-JEOL JEM-6360 Mira-3, Tascan, Republic of Czech.

The optical properties of thin film were examined using UV-visible absorption spectra using a Double Beam UV Spectrophotometer V-750 (Jasco Corp., Tokyo, Japan) scanned at absorption mode with wavelengths in the range of 200–700 nm.

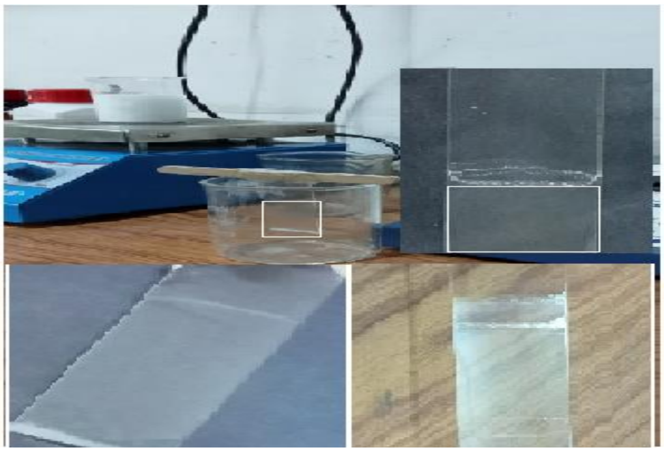

Fig 1 Deposition of $Tio_2$-$Al_2O_3$-$La_2O_3$ Thin Film in Glass Substrate

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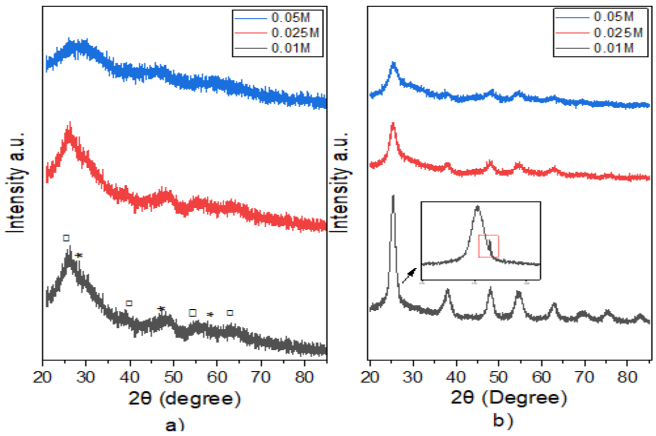


Fig 2 XRD spectra of $TiO_2$-$Al_2O_3$ doped $La_2O_3$with different concentration (a) before annealing, (b) after annealing, where (*) for $La_2O_3$ and (□) for $TiO_2Al_2O_3$

## III. RESULT AND DISCUSSION

### A. *Structural Studies (XRD Analysis)*

Fig. 2 shows the XRD spectra of doped $TiO_2$-$Al_2O_3$ thin film by La at different concentrations (0.01, 0.025, 0.05) M prepared at room temperature. In fig. 2a show the XRD of thin film before annealed the films were shows a small degree of crystallisation (amorphous like) and broad peaks at (100), (002) and (201) orientations correspond to $La_2O_3$ hexagonal phase (JCPDS no: 00-022-0688) [45,46], (101) and (116) corresponding to $TiO_2$-$Al_2O_3$ anatase phase [47].as the concentration of $La_2O_3$ increases the peaks widen further indicating either smaller crystals or an unordered shape containing lanthanum ions, [48]. besides, the intensity of all peaks decreases possibly due to the incorporation of $La^{3+}$ ions into $TiO_2$-$Al_2O_3$ matrix. [49]. After annealing treated at 500° C the intensities of the peaks increase, which means that the enhancement in the degree of crystallinity. The developed film shows a level of crystallinity with two or three peaks credited to $La_2O_3$, as displayed in Fig. 2b, and an increase in the concentration of Lanthanum does not improve the crystallization of the films.

From Debye-Scherrer's equation (1), The average crystallite size was calculated:

$$D = \frac{K\lambda}{\beta cos\theta} \qquad (1)$$

Where D is the average crystallite size, K is the Debye Scherrer's constant (K= 0.94), λ is the wavelength of the CuKα- radiation (λ = 1.5406 Å), β is the full width half maximum (FWHM) of the peak, and θ is the Bragg's angle. The D value of thin film at 3 concentrations (0.01, 0.025, 0.05) M before and after annealed shown in table 1, and the Bragg equation was used to find the spacing between the diffracted planes (2)

$$d = \frac{n\lambda}{2\sin\theta} \qquad (2)$$

Table 1 Change in the Crystal Size (D) and Space Between Diffraction Planes (D) Value before And After Annealing For Different La Concentrations.

| Concentration ( M) | Before annealed | | After annealed | |
|---|---|---|---|---|
| | D (nm) | d (nm) | D (nm) | d (nm) |
| 0.01 | 24.4 | 3.07 | 31.1 | 1.91 |
| 0.025 | 22.6 | 3.13 | 33.6 | 2.20 |
| 0.05 | 21.5 | 3.19 | 22.1 | 2.63 |

### B. *Raman Spectroscopy*

Raman spectrometer is a useful tool for observing the phonon vibration modes of chemical bonds, especially in crystalline samples, Raman study showed the nature of bonding present in the $La_2O_3$ thin film. The Raman spectrum in the wave number range of 50-5500 $cm^{-1}$ is shown in Fig. 3a, four peaks located at 144, 467.26, 596.70, 2414 $cm^{-1}$ and broad peak in the range (3020-360) the first sharp peak located attributed to $TiO_2$ anatas phase in first concentration (0.01M) and it is shifted to less wave number with decreasing intensity when the concentration of La increasing , the peak at 467 $cm^{-1}$ corresponds to the La–O stretching vibrations it is increasing the intensity slightly with increase the La concentration [50,51,49].Third peak at 596.70 $cm^{-1}$ for $TiO_2$-$Al_2O_3$, where the peak at 2414 for alkene (C=C) group and last region for O-H group. After annealed Fig. 3b observed sharp peaks appear corresponding to optimization of the crystal structure in the concentration (0.01M) but after increase the La concentration the peaks faded and turned to one hump that because Raman scattering is limited to near zone centered phonons due to spectroscopic selection rules, in the case of nanostructures, this selection rules relaxed and phonons other than those centered around the region, also contribute due to confinement of phonons in to a crystallite of finite dimensions, this results in a line-shape change in the first-order Raman spectrum which causes wide in the peaks[52]. This results are consistent with that of XRD patterns.

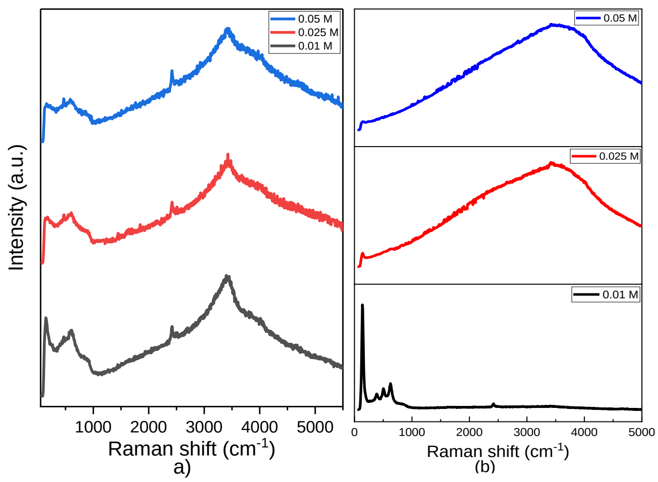


Fig 3 Raman Spectra of $Tio_2$-$Al_2O_3$-$La_2O_3$ (A) before Annealing and (B) After Annealing

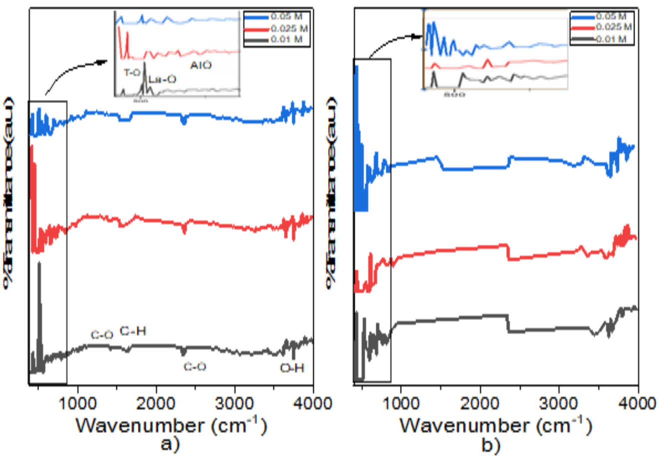


Fig 4 FT-IR Spectra for Tio$_2$-Al$_2$O$_3$-La$_2$O$_3$ Thin Film (A) before Annealing and (B) After Annealing.

### C. *Fourier Transform-Infrared (FT-IR) Analysis*

The FTIR approach showed the chemical composition of the manufactured materials using a wavelength range between 400-4000 cm$^{-1}$, in Fig. 4a show is the FTIR spectrum of TiO$_2$-Al$_2$O$_3$-La$_2$O$_3$, and its observed the three regions at 400-1000 cm$^{-1}$, 3500-4000 cm$^{-1}$, some peaks at wavenumber 1418.39, and 2336.34 cm$^{-1}$ ,first region there are many sharp peaks associated to Ti-O, O-Ti-O and O-Al-O stretching and bending vibrational modes [53,47], the bending vibration of La-O at (508.15, 480 and 669.17 cm$^{-1}$)[54,55][52,49], and stretching of the hydroxyl group(O-H) in the last region at 3500-4000 cm$^{-1}$ , and at ( 1418.38 cm$^{-1}$)[56]. the peak at 2336.34 cm$^{-1}$ can be attributed to the presence of carbonates, that may form when the La$_2$O$_3$ react with CO$_2$ in the air [57], that in the first concentration (0.01M) but when the La concentration increasing notice the intensity of peaks increasing and becomes more sharp. after annealed at 500$^o$ C observed increased of the peaks intensity in first region and the peaks shifted towered the high wave number Fig. 4b [55]

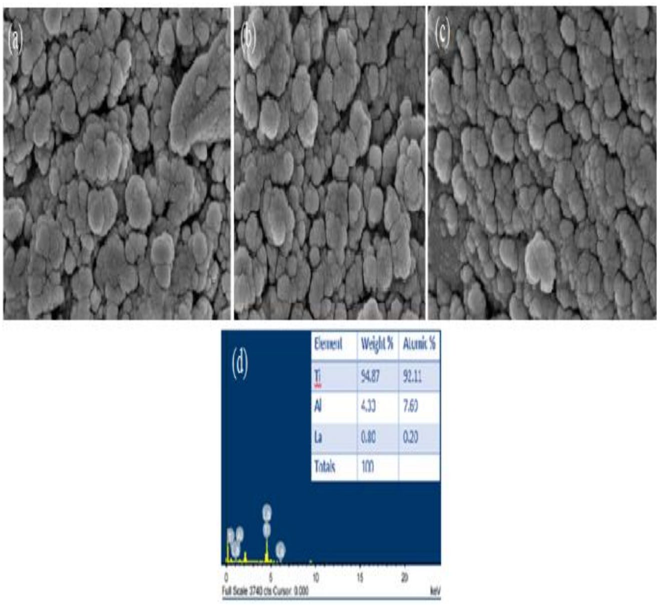


Fig 5 The FE-SEM Images of Tio$_2$-Al$_2$O$_3$-La$_2$O$_3$ Thin Film of Difference Concentration (A 0.01M, B 0.025M, C 0.05) and EDS Spectrum.

### D. *Morphological and Elemental Analyses (FE- SEM &EDS)*

The general morphologies and elemental analysis of the TiO$_2$-Al$_2$O$_3$-La$_2$O$_3$ composed are examined using FE-SEM and EDS respectively, Fig. 5(a, b and c) shows micrographs of TiO$_2$-Al$_2$O$_3$- La$_2$O$_3$ thin films, the surface of substrate is covered.

Table 2 E$_g$ Values for Tio$_2$-Al$_2$O$_3$ and Tio$_2$-Al$_2$O$_3$-La$_2$O$_3$ in Different Concentrations of La.

| Samples | Before annealing | After annealing |
|---|---|---|
| | E$_g$ ev | Eg ev |
| TiO$_2$-Al$_2$O$_3$ * | 3.32 | 3.14 |
| TiO$_2$-Al$_2$O$_3$-La$_2$O$_3$(0.01M) | 3.57 | 3.45 |
| TiO$_2$-Al$_2$O$_3$-La$_2$O$_3$(0.025M) | 3.27 | 3.13 |
| TiO$_2$-Al$_2$O$_3$-La$_2$O$_3$(0.05M) | 2.98 | 2.90 |

Uniformly with three-dimensional particles of TiO$_2$-Al$_2$O$_3$- La$_2$O$_3$ thin film., [58,45], observed that the images appear as a cluster of tiny spherical grains and the films were homogeneous and approximately uniformly deposited over the substrate surface, notes that the particles diameter decreases in due to an increase in La concentration [59,60]. and this result is consistent with the result obtained in the XRD analysis.

The EDX analysis of TiO2-Al$_2$O$_3$-La$_2$O$_3$ (Fig.5d) indicated that the chemical composition consisted of Ti (92.11), Al (7.69), and La (0.20) %. These data confirm that the demonstrating of successful deposed of TiO$_2$-Al$_2$O$_3$-La$_2$O$_3$ nanoparticles on the surface of the substrate.

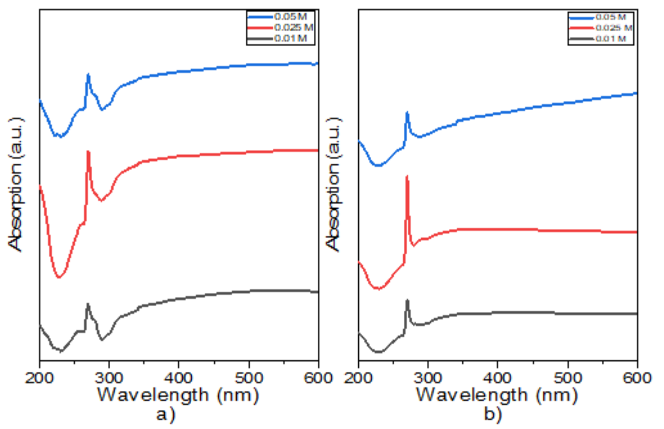


Fig 6 UV-Vis Absorption Spectra of Tio$_2$-Al$_2$O$_3$-La$_2$O$_3$ Thin Film(A) Before Annealing and (B) After Annealing.

### E. *Optical Study (UV-Vis Analyses)*

Fig. 6a shows UV-vis absorption spectra of (TiO$_2$-Al$_2$O$_3$-La$_2$O$_3$) samples with different (La) concentration (0.01, 0.025, 0.05M) before annealed. The spectrum shows a sharp adsorption band from 263 to 285 nm with variation in intensity and peak width with change of Lanthanum concentration, in Fig. 6b (after annealed) observed that the spectra of (TiO$_2$-Al$_2$O$_3$-La$_2$O$_3$) samples annealed at 500 C shows more intense sharper absorption in the same range with variation in intensity with change of Lanthanum concentration. the concentration (0.025M) of Lanthanum shows the highest intensity in both cases before and after annealing. The bandgap (Eg) Calculation was performed by fitting the UV-Visible absorption data with the direct transition equation by extrapolating the linear portions of the curves to an absorbance equal to zero (Tauc's formula). for all synthesized samples as shown in Fig. 7 when doped with lanthanum a decrease in the value of (Eg) was observed with an increase in (La) concentration in both cases before and after annealing if compared to the energy gap values in the case of ($TiO_2$-$Al_2O_3$). [47]. The observed results clearly indicate that there is decrease in the bandgap values with lanthanum doping. [61,62]. Table. 2 and fig.8.

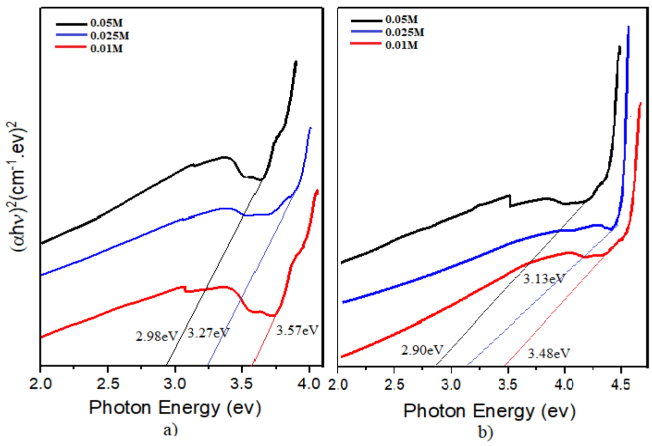


Fig 7 Band- Gap Energy of $TiO_2$-$Al_2O_3$ –$La_2O_3$ before and after Annealing

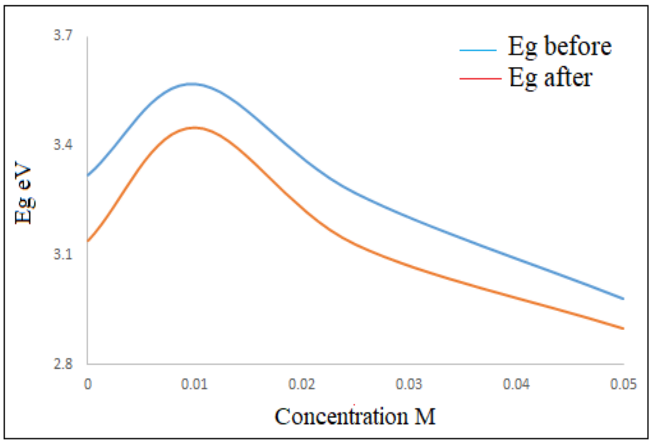


Fig 8 Band- Gap Energy of $TiO_2$-$Al_2O_3$ –$La_2O_3$ Various with La Concentration before and after Annealing

## IV. CONCLUSION

In conclusion, the 3D particles of $TiO_2$-$Al_2O_3$- $La_2O_3$ thin film with a hexagonal crystal structure was successfully synthesized by using Ti $[OCH(CH_3)_2]_4$ (TTIP), ($AlCl_3$. $6H_2O$) and ($LaCl_3$.7($H_2O$), it is clear that the preparing of $TiO_2$-$Al_2O_3$-$La_2O_3$ using CBD method produce an improved character of the sample due to the decreasing impurities and releasing a compact sample with a better band-gap sample which influencing the sample properties. Where the annealed sample show a cute, sharp and pure sample. The FTIR and Raman analyses prove this improvement of properties. The band-gap value (3.57, 3.27, 2.98) eV before annealing and (3.45, 3.13, 2.90) eV after annealing with increasing the La concentration support this conclusion.

We recommend to study several concentrations with different preparation methods to get improved properties of $TiO_2$-$Al_2O_3$-$La_2O_3$ sample.

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