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# Structural and optical investigation of manganese oxide thin films by spray pyrolysis technique

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Thin films of MnO are well suited for opto-electronic applications, such as solar energy conversion due to its optical and electrical properties as well as its chemical and mechanical stability. MnO thin films were prepared on glass substrate using a simple and low-cost chemical spray pyrolysis at different substrate temperature. The MnO films were characterized by X-ray diffraction (XRD), photoluminescence (PL) and ultraviolet-visible (UV-VIS) optical spectroscopy. The XRD pattern reveals that MnO films possess cubic structure, the average crystallite size was 26.509 nm. Photoluminescence activity of the sample was carried out. The optical band gap was calculated and compared to the band gap energy determined from the optical transition involved in the material and is found to be 2.33eV.

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*Keywords:* Manganese oxide, Spray pyrolysis , XRD, Band gap, PL spectra

## 1. Introduction

Manganese oxide (MnO) is a transitional material having interesting physical and chemical properties. It has triggered opto-electronic applications. It is used as electrode materials [1, 2], electrochemical capacitors [3, 4], rechargeable batteries, catalysts, sensors [5], magneto-electronic devices [6]. MnO was used as a substrate in the synthesis of magnetic oxide perovskite compounds, which have a variety of electrical and magnetic properties like metal-insulator transistors and a colossal magneto resistance [7-9]. MnO of different structures are deposited using several techniques such as sol-gel [6], thermal evaporation in vacuum [10], MOCVD [11]. Manganese oxide of different structure (MnO, $Mn_2O_3$, $MnO_2$ and $Mn_3O_4$ ) are usually prepared by varying calcinations condition of starting chemical precursor bulk or film . They can also be prepared each other by varying the temperature and atmosphere (vacuum or air, oxygen, hydrogen etc.,) of the calcinations [11]. MnO are prepared in the form of thin films on glass substrate by chemical spray pyrolysis technique and their structural and optical properties are discussed.

## 2. Experimental procedure

MnO thin films were grown on glass substrate using a typical spray pyrolysis technique. The spraying solution was prepared by dissolving 0.1 mole of manganese chloride in double distilled de-ionised water along with 2 to 3 drops of HCl. The substrate temperature was maintained at 350 ºC and 450 ºC (± 2 ºC) through a thermocouple (Pt-100) as a sensor for temperature controller. Purified air was used as a carrier gas and it was maintained at 0.4 kg/cm$^2$ with constant flow rate of about 3ml/min. The nozzle to substrate distance was kept at 30 cm. The rate of MnO thin film formation takes place as follows

$$MnCl_2 + H_2O \rightarrow MnO + 2HCl$$

The MnO films were subjected to X-ray diffraction technique to investigate the structural properties using a JEOL JDX service having $CuK_\alpha$ radiation ($\lambda$ = 1.5406 Å). Transmittances versus wavelength measurements were made using Carry 500 Varian UV-VIS-NIR spectrophotometer. FP-6500 spectrofluorometer was used to record fluorescence spectrum.

## 3. Results and discussion

### 3.1 Structural analysis

The structural elucidation of MnO film was shown in Fig. 1. The diffraction pattern exhibit peaks at $2\theta$=36.5587˚, d=2.4579Å; $2\theta$=38.1193, d=2.3608Å; $2\theta$=56.03˚, d=1.6398Å; $2\theta$=68.5735, d=1.3712Å and $2\theta$=73.7512˚, d=1.2836Å was identified to be (111), (200), (220), (311), (222) planes having cubic structure with lattice parameter a=4.36084Å which is in agreement with literature value of 4.445Å [12]. The existence of shift in some peaks is due to internal strain existing in the crystallites due to disproportionate array of the constituents [13]. The microstrain is calculated using the formula $\varepsilon = \beta\cos\theta/4$ and the average strain was found to be 0.0472. The crystallites size is deduced from Debye-Scherrer formula $D=k\lambda/\beta\cos\theta$ [14], where $\beta \rightarrow$ the broadening of diffraction line measured at half of its maximum intensity, λ→X-ray wavelength (1.5406 Å), θ→Bragg angle, k→constant (0.9).The calculated average crystallite size was 26.509 nm.

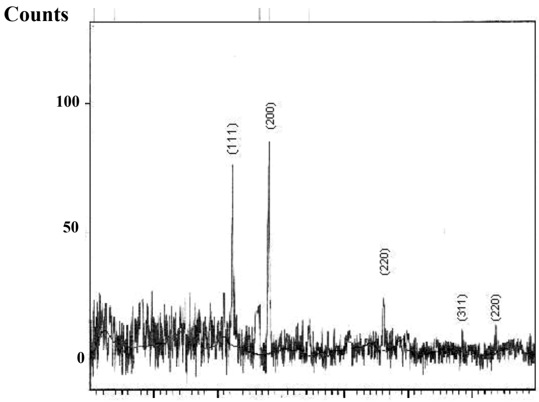


*Fig.1. XRD pattern of MnO thin film.*

### 3.2 Transmittance analysis

The UV-Vis spectrum for MnO thin film was recorded in the range of 300-1200 nm as shown in Fig.2. The film deposited at 400ºC shows 10% of increase in transmittance compared to 350ºC. This increase in transmittance is due to decrease in thickness of the film as substrate temperature increases from 350ºC to 400ºC. The absorption co-efficient (α) and band gap energy ($E_g$) were calculated from the transmission spectra using the relation α= [(-2.303/d) log (1/T)]. Where, d→ thickness of the film, T→ observed transmittance. A typical plot of $(\alpha h\nu)^2$ Vs (hν) is shown in Fig.3. Extrapolation of linear portion of the curve to $(\alpha h\nu)^2 = 0$ gives the band gap value $E_g$= 2.2 eV for 350ºC and 2.25 eV for 400ºC respectively .

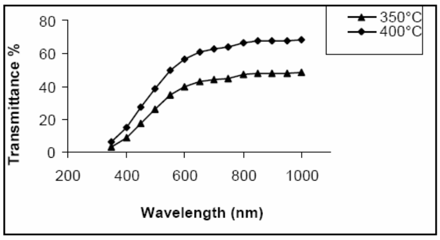


*Fig. 2.The Transmittance spectra of MnO films.*

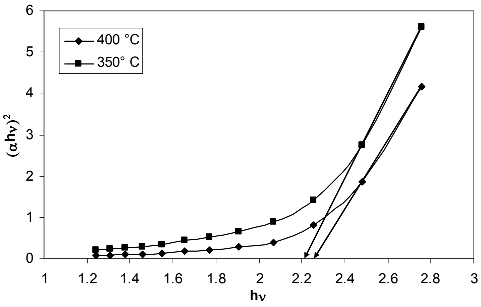
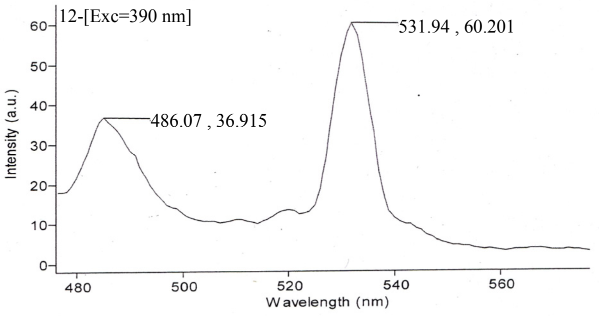


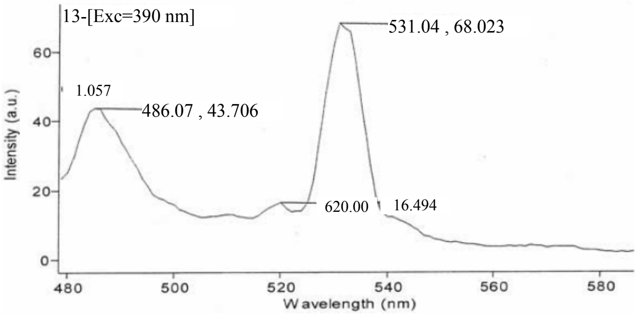
*Fig. 3. Energy band gap of MnO thin films.*

### 3.3 Photoluminescence analysis

The spectrum emitted by the radioactive recombination of photogenerated minority carriers is a direct way to measure the band gap energy. However, large amount of impurities induces a large free carrier density in the bands. Consequently, a different carrier interaction causes remarkable modification of the line shape and spectral energy of the PL feature [15]. The excitation and emission spectra of MnO were recorded. The excitation spectrum was recorded in the range of (380-395) nm as shown in Fig. (4.1), (4.2). The sample was excited at 389nm, a peak at 485 and 531nm was observed in the emission spectrum. The result indicates that MnO films have blue and green fluorescence emission. The band gap was calculated using the formula $E_g$=hc/λe, where h, c and e are constants, λ→ wave length of fluorescence. The calculated band gap energy was about 2.336eV.



*(a)*



*(b)*

*Fig . 4. (a)PL spectrum of MnO thin film at 350° C; (b) PL spectrum of MnO thin film at 400° C.*

## 4. Conclusions

MnO thin films were prepared using by spray pyrolysis technique. The structural analysis revealed the cubical nature of the film with average crystallite size 26.509nm. The photoluminescence study shows intensity increment with increasing substrate temperature possessing blue and green fluorescence. The band gap obtained from PL and UV-Vis was found to be ~ 2.33eV.

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