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STUDY OF STRUCTURAL & OPTICAL LUMINESCENCE BEHAVIOR OF CdO:Mn SYSTEM FOR ENERGY APPLICATION

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ABSTRACT

CdO thin films with and without Mn doping were deposited on glass substrates using sol-gel method at room temperature. The effect of Mn content (1,3,5 wt %) on the optical, structural and morphological properties were studied. X Ray diffraction patterns shows that all the films are single phase and have cubic structure with (200) preferential orientation along c axis. Presence of functional group and chemical bonding as well as the surface changes on the particle determined by the FTIR spectra. Result of optical spectra shows that band gap decreases as increases the 1 at % Mn doping concentration and band gap increases with increasing 3 and 5 at % of Mn concentration. Photoluminance (PL) Spectra shows the broad peak in nearly U-V region with longer wavelength at 342, 343, 342 and 332 nm respectively have been found.

Key words:- Thin film, Spin coating, Photoluminance, X Ray diffraction, FTIR Spectra,

1. Introduction:-

The II-VI group conducting materials such as cadmium selenide (CdSe), cadmium telluride (CdTe), zinc selenide (ZnSe), cadmium oxide (CdO), zinc sulfide (ZnS), and zinc telluride (ZnTe) have wide and remarkable application in various field. Cadmium oxide have been preferable consideration due to its various useful applications such as gas sensors, photovoltaic photo diodes and transparent electrodes, etc. due to its low resistivity, high carrier concentration and high optical transmittance in the visible region of solar spectrum. (M.Thirumoorthi et al 2015), (Mafiana Edward et al 2020). Cadmium oxide has much higher capacity for absorption and emission of radiation (Nida Kati , 2018). It is n-type

semiconductor. The conductivity of cadmium oxide is nearly conductivity of metals (Mafiana Edward et al 2020) and the band gap is about 3.4 eV, large excitation binding energy is about 60 meV at room temperature (Shenghong Yang et al 2013). It has very short luminescence and high optical gain of about 300 cm^{-1} which are required for various optoelectronics and magneto-optical devices (Shenghong Yang 2013). CdO is cubic structure with each ion surrounded by six ions of opposite electric charge, octahedrally arranged (Adel H. Omran et al 2015), (Metin Kul et al 2007). Optoelectronic properties of CdO with doping of different metallic ions have been studied by many researchers such as Tin (M.Thirumoorthi et al 2015), Indium (R.K. Gupta et al 2008), Aluminum (I.S. Yahia et al 2013), Gallium (R J Deokate et al 2010) and Manganese (K.Sankarasubramanian et al 2014). Physical properties of Mn doped CdO thin films have already been reported by some researchers. Study of Microstructure and Electrical properties of Mn doped CdO thin film prepared by home built spray pyrolysis techniques carried out by S. Amutha et al. (S. Amutha et al 2012). They observed that grain size decreases as increasing the concentration. XRD study of Mn doped CdO thin film prepared by SILAR method and investigated by (M. Mahabood et al 2020), are polycrystalline nature of the film with preferential orientation along (111) plane.

2. Experimental Techniques

Nanocrystalline thin films of pure and Mn doped CdO, were synthesized by preparing the starting sol of suitable consistency. The precursor solution was prepared by mechanical mixing by mortar pestle for 60 min. of 0.7812 g of $CdO_{1-x}Mn_x$ (x = 0.00, 0.01, 0.03, 0.05) and then added 10 ml dichloromethane (CH_2Cl_2) as a solvent. The prepared solution was stirred continuously for one hour at 60°C. Now this solution is prepared for spin-coating process. The glass substrates used for coating purposes were first cleaned in a mixed solution of HNO_3 and HCl and again rinsed in distilled water and ethanol for two-three times. The glass substrates were further dried and a thin uniform $CdO_{1-x}Mn_x$ (x = 0.00, 0.01, 0.03, 0.05) film was deposited by a spin coater rotated with a maximum speed of 800 rpm for 30 s. Prepared each sample of $CdO_{1-x}Mn_x$ (x = 0.00, 0.01, 0.03, 0.05) annealing for 24 hrs with temperature at 60°C.

The film is investigated by X-ray diffractometer (Bruker AXS, CuKα 1.54060 Å) in 2θ range of P L spectra of sample, analyzed from UV visible spectroscopy (make - Shimadzu UV -2600) in the range of 200 – 500 nm. The band gap of thin film was calculated by analyzing the optical absorption spectra obtain by UV visible spectroscopy (make - Shimadzu UV -2600). The surface morphology of the sample was investigated by Field Emission Scanning Electron Microscope (make - JEOL make JSM-7610F

Plus FESEM). The chemical composition of the synthesized materials was analyzed by FTIR (make-Bruker Alpha FTIR Spectroscopy.

3. Result and Discussion:-

3.1 XRD Study

Structure studies were carried out to confirm the crystallinity, by X-ray diffractometer with CuKα radiation (λ = 1.5418 Å) in the range of 5º to 80º. The X-ray diffraction patterns of thin film of $CdO_{1-x}Mn_x$ (x = 0,.01,.03,.05) deposited on quartz substrate are shown in figure 1. All of the sharp and different peaks of the XRD patterns indicate polycrystalline in nature with diffraction patterns at 2θ = 32.62°, 38.01°, 54.89°, 65.76° and 69.01° indexed as (111), (200), (220), (311) and (222) planes according to JCPDS Card No. 73-2245 (N. Manjula et al 2015). It is observed that the result of samples shows the cubic structure along preferential orientation (200) planes. In other studies, preferential orientation found along (111) planes. It can be due to the difference in growth method (Harun Guney 2018). It was found that all of the diffraction peaks belonged to CdO with the increasing ratio of Mn dopant, the crystal structure remained the same and only the peak intensities changed. This can be interpreted that Mn is homogeneously distributed in the CdO structure and Mn ions can exchange. It was concluded that the samples were produced in high purity Mn ions replaced the CdO atoms without changing the crystal structure (Ugur Caligulu et al 2021). Value of inter-planer distance (d) of undoped and Mn doped CdO thin films were calculated using Bragg's law and shown in table 1. Peak (200) is consider as the main peak and this peak was considered for the calculation of lattice constant also. The lattice constant and volume of the unit cell (V) for cubic CdO calculated from (200) main peak using the following equation (Harun Guney 2018).

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$V = a^3$$

The calculated 'a' values of undoped and Mn doped CdO were found 4.726 Å, 4.722 Å, 4.726 Å and 4.747 Å respectively. Calculated V values were found as 105.56 $Å^3$, 105.29 $Å^3$,105.97 $Å^3$ and 106.97 $Å^3$ respectively. Crystallite sizes of the deposited films obtained using Debye-Scherer's equation given in equation by (Mafiana Edward et al 2020)

$$D = \frac{0.9\,\lambda}{\beta cos\theta}$$

The crystalline size of pure and Mn doped (1%, 3%, and 5%) CdO thin films calculated at (111) lattice are fond 29.43 nm, 32.32 nm, 29.42 nm and 19.03 nm respectively. This range of crystallite sizes confirmed that the deposited films are nano-films of Manganese doped Cadmium oxide (CdMnO2). The result obtained is in line with result obtained by (Mafiana Edward et al 2020).

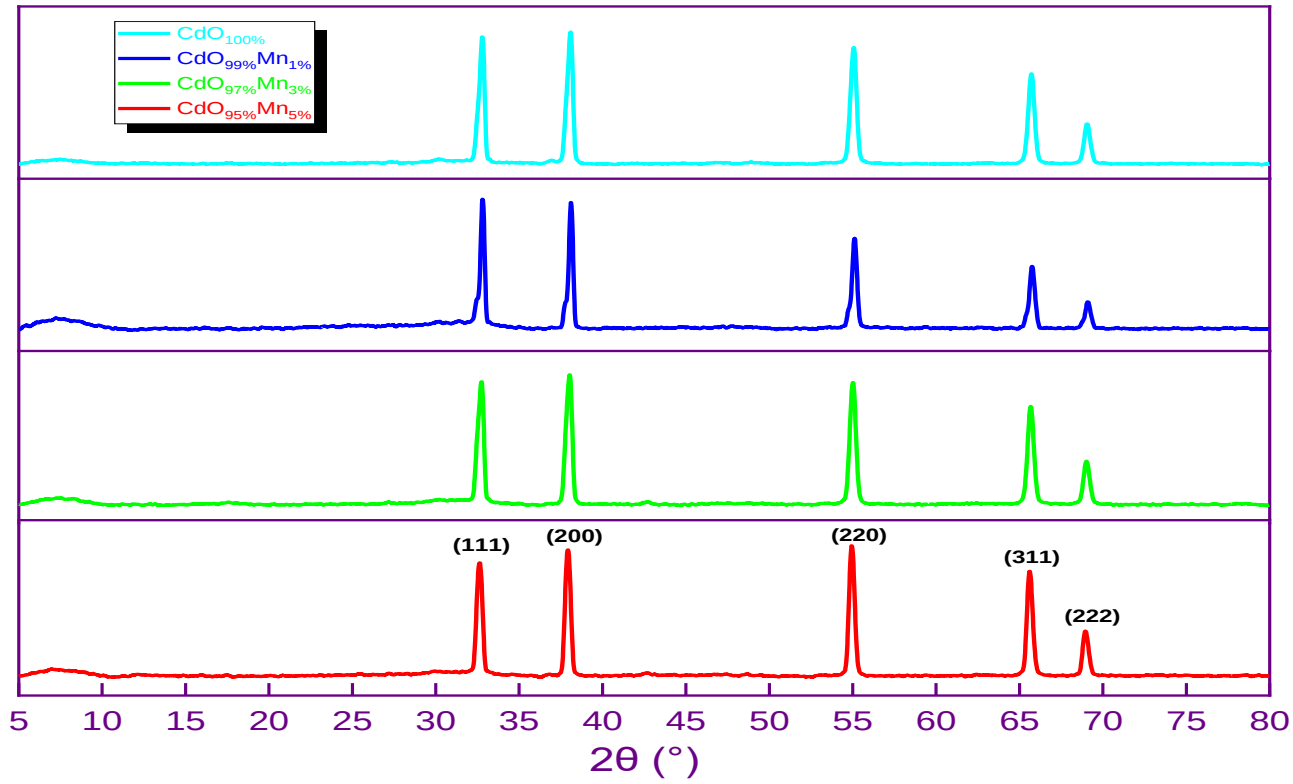


Figure 1:- X- ray diffraction pattern of pure and Mn-doped CdO thin films.

Sample	hkl	Position (°2θ)	FWHM (°2θ)	d-spacing (Å)	a (Å)	V $(Å)^3$
CdO	(111)	32.8302	0.2814	2.728	4.726	105.56
	(200)	38.1229	0.2814	2.361		

	(220)	55.0875	0.4349	1.667		
	(311)	65.7184	0.3838	1.421		
	(222)	69.0475	0.3582	1.36		
1% Mn doped CdO	(111)	32.222	0.2558	2.72872	4.722	105.29
	(200)	38.1206	0.2814	2.36076		
	(220)	55.1125	0.2814	1.66646		
	(311)	65.7314	0.307	1.66646		
	(222)	69.0786	0.2558	1.66646		
3% Mn doped CdO	(111)	32.7946	0.2814	2.73095	4.726	105.56
	(200)	38.084	0.5117	2.36294		
	(220)	55.0422	0.4349	1.66842		
	(311)	65.6722	0.4093	1.42177		
	(222)	69.0043	0.3838	1.36103		
5% Mn doped CdO	(111)	32.7193	0.4349	2.73708	4.747	105.97
	(200)	38.9068	0.4349	2.37358		
	(220)	54.9173	0.4093	1.67192		
	(311)	65.5794	0.3838	1.42356		
	(222)	68.906	0.3838	1.36273		

Table 1:- Calculated 'a' and 'v' value of pure and Mn doped thin films.

3.2 FTIR Analysis

FTIR spectra of $CdO_{1-x}Mn_x$ (x=0.00, 0.01, 0.03 and 0.05) is analyzed to determine the presence of functional group and chemical bonding as well as the surface changes (shown in figure 2). These analyses can reveal the quality or consistency of sample. FTIR transmission spectra were obtained using a Burker Alphas spectrometer from 4000 – 500 cm^{-1} using 0.8 cm^{-1} resolution. In FTIR spectrum, various peaks corresponding to the main absorption band can be seen. The medium broad absorption bands at 3848 cm^{-1} and strong absorption band at 3742 cm^{-1} represent the O-H stretching of the Hydroxyl group. The broad absorption peak at around 3400–3600 cm−1 is attributed to normal

polymeric O H stretching vibration of H_2O in CdO lattice (M. Thirumoorth et al 2015). Sharp and strong band at 1525 and 1694 cm^{-1} belongs to the Cd-O vibration and confirms the formation of CdO (R. Aydin et al 2019). The absorbance peaks appeared in the fingerprint region between 700 cm^{-1} and 400 cm^{-1} at 687, 580, and 524 cm^{-1}. These absorption peaks produced due to the presence of the functional group Cd-O structure. (Ayman M et al 2020).

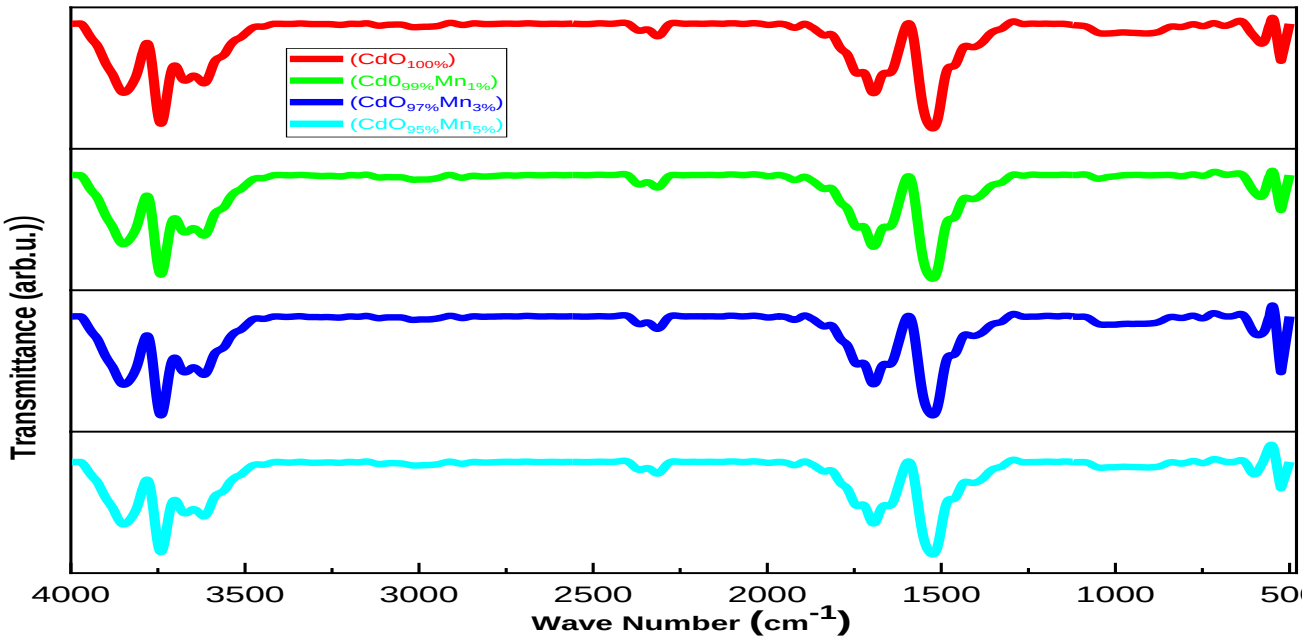


Figure 2:- FTIR Spectrum of $CdO_{1-x}Mn_x$ (x = 0,1,3,5)

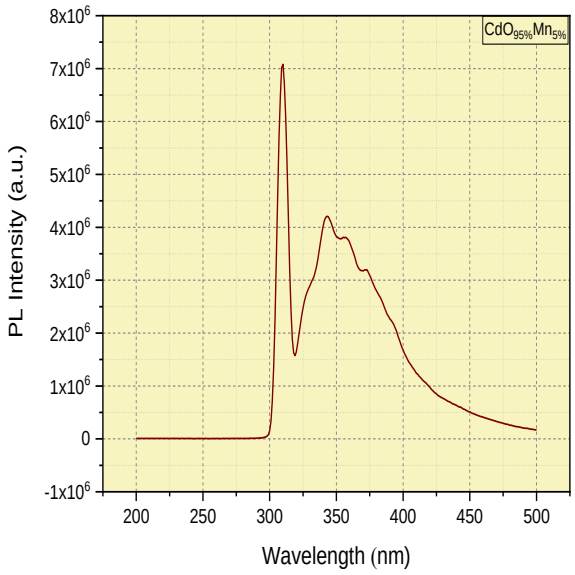
3.3 PL Study

Optical crystalline quality of pure and Mn doped CdO was evaluate by UV visible spectral photometry P L spectroscopy. Structure defects and the band gap energy of pure and Mn doped CdO thin film was analysis at room temperature was carried out by P L spectra. Pure and 1,3,5 wt% Mn doped sample have a week ultraviolet emission peak centered at about 309, 309, 310 and 309 nm found respectively. The absorption has increased after doping, this may be due to the introduction of the Mn defect states within the forbidden band which may lead to absorption of incident photons. These peaks may be because of Shockley–Read–Hall recombination and indicate the defect of crystal.

The broad peak in nearly visible region with longer wavelength at 342, 343, 342 and 332 nm respectively have been found. The peaks in the U-V region corresponds to near band edge emission (NBE) and shows the

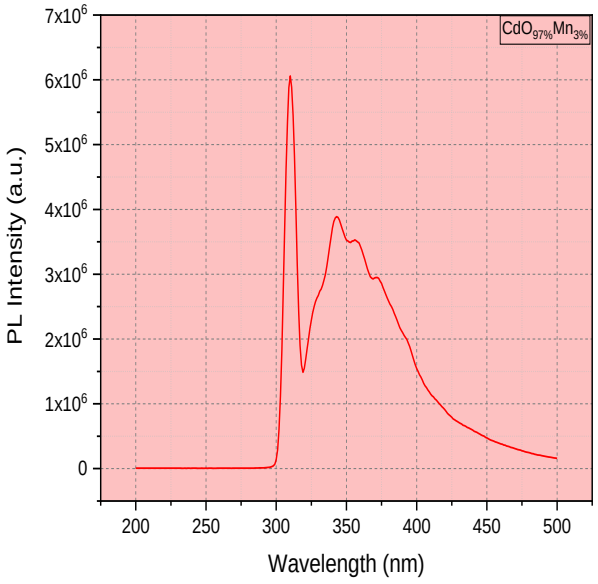
Auger recombination. The position of absorption spectra is shifted towards the lower wavelength and known as blue shifted which correlated to the change in the optical band gap value (M. Anitha et al 2019)

From this figure, it is cleared that there is emission peak centered around 342-343 nm in all cases, which corresponding to the U-V region emission produced from electronic transitions of ionized oxygen vacancies due to deep level of conduction band to valence band, while in the case of doping with Mn, there is significantly decreased in the intensity as compared to that in the pure CdO thin film, which is relate to excitation at certain new stated coming from impurities ions of Mn. This significant decrease may be happened due to increasing the amorphous nature or the presence of impurity states formed from Mn structure in this case, the rate of electron-hole recombination becomes lower that in the pure CdO thin film. (A.A. Menazea et al 2020)

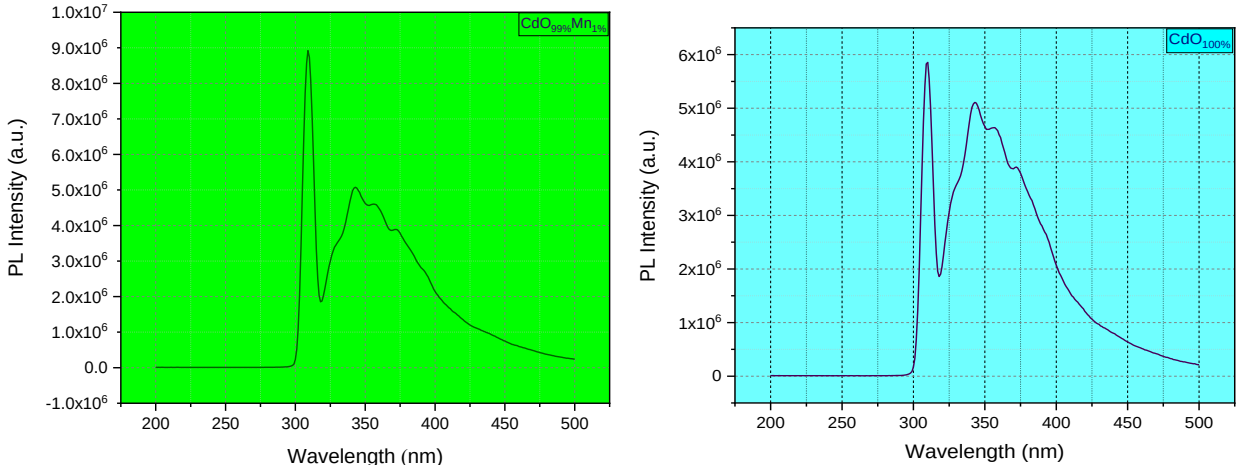


PL Intensity v/s Wavelength graph of pure CdO thin film.

(b)



PL Intensity v/s Wavelength graph of 1% Mn doped CdO thin film.



PL Intensity v/s Wavelength graph of 3% Mn doped CdO thin film.

PL Intensity v/s Wavelength graph of 5% Mn doped CdO thin film.

Figure 3:- PL Intensity v/s Wavelength graph

Figure 3 shows the optical band gap of pure and Mn doped CdO thin film. UV-visible spectrophotometry leads to observe the effect of Mn doping on the band gap of synthesized films. The relation between absorption coefficient (α) and photon energy (hν) is expressed as follows (M.Karunakaran et al 2019)

$$\alpha h\nu = A\,(h\nu - E_g)^{m/2}$$

where A is the energy dependent constant, E_g is the optical band gap of the material, m is a constant that depends on the semiconducting materials and m=1 for direct transition whereas for indirect band gap semiconductor m=4. The linear region of the $(\alpha h\nu)^2$ against hν plot is extrapolated to intersect the energy axis, since $E_g = h\nu$ (direct band gap) when $(\alpha h\nu)^2 = 0$. The estimate value of E_g have been presented in table 1. The obtain value of E_g for undoped CdO thin film is 2.57 eV. The band gap of 1 at % Mn doped CdO found decrease but it is found increased as increased 3 and 5 at % of Mn concentration. The band gap of undoped CdO was found 2.57 eV and it decreased to 2.54 eV with increasing 1 at % Mn doping and increased 2.65 eV for 3 and 5 at % Mn concentration. This result is revel with XRD result. Decrement in band gap 2.47 to 2.21 eV was also found by N. Manjulata et al 2015. N. Manjulata et al. [2015] observes that the decrease in the optical band gap with the increased Mn doping could be related to the structural deformation in the CdO films caused due to the replacement of either subsituational or interstitial cadmium ions in the CdO lattice.

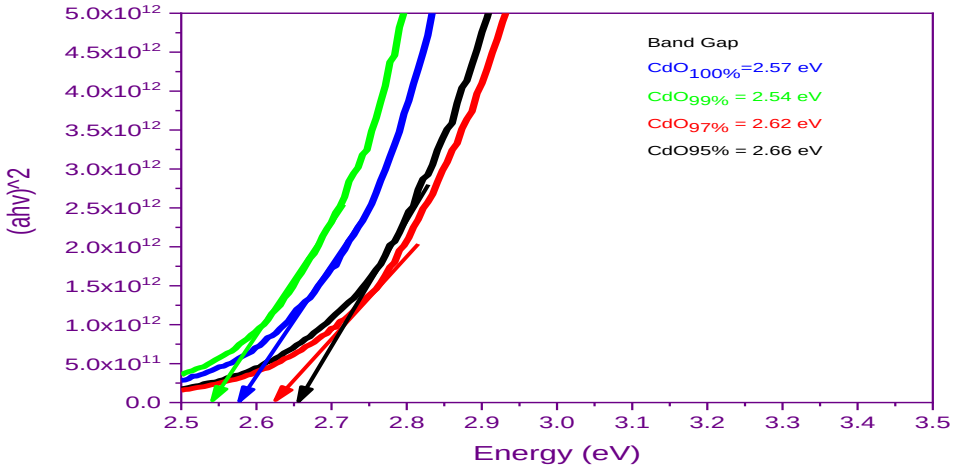


Figure 4:- $(\alpha h\nu)^2$ as a function of photon energy for undoped and 1, 3 and 5 at% Mn doped CdO thin films.

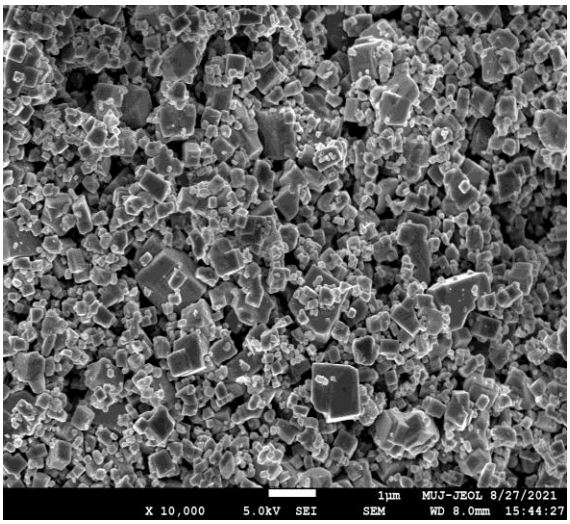
S. No.	Materials ($CdO_{1-x}Mn_x$)	Band gap (E_g)
1	$CdO_{100\%}$	2.57 eV
2	$CdO_{99\%}$ $Mn_{1\%}$	2.54 eV
3	$CdO_{97\%}$ $Mn_{3\%}$	2.62 eV
4	$CdO_{95\%}$ $Mn_{5\%}$	2.65 eV

Table 2:- Determination of Band gap of pure and Mn doped CdO thin films

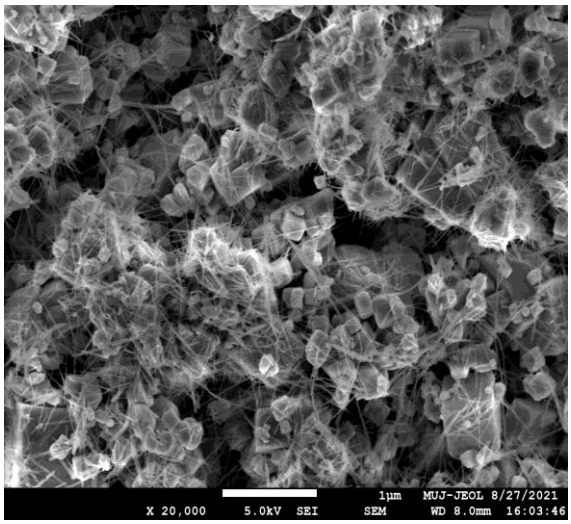
3.4 SEM Analysis

Morphological study has been done by scanning electron microscope (SEM). Figure 5 shows the SEM micrographs of pure and Mn doped CdO thin films. In this image, pure CdO thin film multiple cubic sized particles are seen with some bulk particles. For 3% Mn doped thin film different sized of cubic particles are found with spread of nano rods all over the sample. Appearance of nano rods has great importance due to heigh specific surface area and applications in various fields. {K. Usharani et. al. 2018}. As Mn concentration increased to 5%, structure is again multiple size particles having less number of bulk

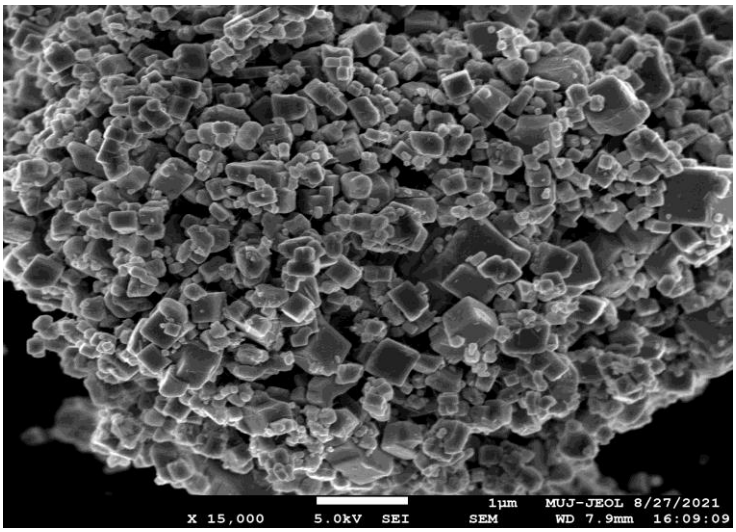
particles then pure CdO sample. These results infer that surface morphology of thin film is affected by Mn doping. Result of SEM analysis pocess a good agreement with XRD results.



(a)



(b)



(c)

Figure 5:- SEM images of (a) Undoped CdO (b) 3 at % Mn doped (c) 5 at % Mn doped Cdo thin films

Conclusion

Mn doped CdO and pure CdO films are prepared using sol-gel spin coating technique.

The XRD results shows that the crystals are cubic structure along preferential orientation (200) planes and no formation of secondary phases are there.

The presence of functional groups and chemical bonding was determined by FTIR study.

The photoluminescence spectra of $CdO_{1-x}Mn_x$ (x=0.00, 0.01, 0.03 and 0.05) films have a similar U-V emission. The PL intensity was changed with increasing Mn doping. PL measurements showed that both CdO and Mn doped CdO samples have emissions in U-V region.

The band gap of CdMnO thin film decreased in comparison with pure CdO thin film with increasing 1 at % Mn content and increased with increasing 3 and 5 at % Mn concentration. After doping Mn, the thin film have a better conductivity than that of pure CdO thin film because of abundant carriers.

SEM results infer that the particle is cubic structure and surface morphology of thin film is affected by the increment of Mn doping.

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