

# The effect of silver (Ag) dopant on the structural and optical properties of sol gel prepared CdO nanoparticles

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**Abstract.** Samples of undoped CdO and 5% Ag doped CdO nanoparticles were prepared by sol-gel method and annealed for 1h at various temperatures ranging from 100 – 500 °C. The prepared samples were characterized using XRD, UV-Vis, Photoluminescence and SEM. The results showed that for 5% Ag-CdO, the nanoparticles were completely crystallized at the annealing temperature of 400 °C. Almost similar lattice parameters were obtained for both the undoped and Ag doped CdO nanoparticles. Ag dopant appears to reduce the average grain size of CdO, although it increased as the annealing temperature was raised. Introduction of Ag in CdO resulted in the band gap widening and an increase in the recombination rate.

## 1. Introduction

Nanocrystalline oxides have attracted much attention recently due to their technological importance in solar cells, chemical sensors and liquid crystal displays [1]. CdO is an n-type semiconductor with an FCC structure and has a band gap of between 2.2 eV and 2.7 eV [2]. It has promising applications in a wide range of fields such as solar cells, transparent electrodes, phototransistors and gas sensors [3]. Previous studies have shown that when a dopant has an atomic radius smaller than that of Cd<sup>2+</sup> (0.97Å), the electrical conductivity of the doped CdO increases and the lattice unit cell compressed [4]. Impurities of high ionic radii are expected to decrease the impurity diffusion towards the p–n junction and are therefore important in the fabrication of solar cells and diodes [5]. In this contribution, focus will be on the effect of doping CdO nanoparticles with Ag (1.26Å) which is a high ionic radius impurity in order to understand the structural and optical properties.

## 2. Experimental

### 2.1. Sample preparation

The undoped and 5% Ag doped CdO nanoparticles were prepared using the precursors cadmium acetate dihydrate, 2-methoxyethanol, silver nitrate and ethanalamine. For the undoped CdO, cadmium acetate dihydrate (0.5M) solution was dissolved in 2-methoxyethanol (0.5M) at a constant magnetic stirring for 10 min. For the Ag doped CdO, cadmium acetate dihydrate (0.5M) and 5 wt.% silver

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nitrate solutions were dissolved in 2-methoxyethanol (0.5M) with a constant magnetic stirring for 10 min and then the ethanalamine (0.5M) solution was added drop by drop into both the undoped and the doped solutions separately with continuous stirring. The final solutions were stirred for 2 h at room temperature. The solutions were then allowed to age for 24 h and then filtered to dry. The precipitates for both the undoped and doped CdO were annealed at different temperatures (100, 200, 300, 400 and 500 °C) for 1h.

## 2.2. Sample characterization

X-Ray powder diffraction (XRD) results were obtained using a Philips Analytical X-Ray B.V diffractometer using  $\text{CuK}\alpha$  ( $\lambda = 0.15405\text{nm}$ ) radiation. The average grain size was calculated using the following familiar Scherrer equation:

$$\beta_{(hkl)} = \frac{K\lambda}{D\cos\theta} ,$$

where  $\beta_{(hkl)}$  is the full width at half maximum,  $D$  is the grain size,  $K$  is a constant  $\lambda$  is the wavelength and  $\theta$  is the diffraction angle from the XRD pattern.

The strains ( $\varepsilon$ ) were determined using the following equation:

$$\varepsilon = \frac{\beta_{(hkl)} \cos\theta}{4\sin\theta} .$$

Ultraviolet-visible (UV-Vis) absorption spectra were recorded using a Perkin-Elmer Lambda 750S UV/Vis spectrometer. Photoluminescence (PL) measurements were carried out using Perkin-Elmer LS 55 Fluorescence spectrometer. The scanning electron microscopy (SEM) images were captured using a JEOL-JSM-7500F microscope at a scale of 100nm and a magnification of  $\times 75$ .

## 3. Results and discussions

### 3.1. X-ray diffraction

The XRD patterns of the 5% Ag doped CdO samples calcined at 100, 200, 300, 400 and 500 °C are shown in figure 1. The patterns of the undoped CdO sample preheated at 400 °C is included for comparison purposes. As can be observed in the figure, the samples heated at 100 and 200 °C do not show any peaks associated with CdO. CdO peaks only start to appear at 300 °C although at this temperature there are still peaks associated with the precursors. The sample completely crystallises to CdO at 400 °C. This behavior was also observed for the undoped sample. The XRD profile of the sample calcined at 400 °C displays only three main CdO peaks at  $2\theta = 33.07^\circ$ ,  $35.34^\circ$  and  $55.31^\circ$  associated with the plane (111), (200) and (220); respectively. This is consistent with the values in the standard card (JCPDS No 05-640) as well as the work by Dakhel AA [2].

The average grain sizes, lattice parameters and strains for undoped CdO and Ag doped CdO samples are shown in table 1. A comparison of the average grain size of the undoped sample ( $\sim 51$  nm) and that of the doped sample ( $\sim 40$  nm), both preheated at 400 °C shows that the introduction of Ag does reduce the grain growth. The results of the doped sample show that the average grain sizes increase as the temperature increases. This was also observed for undoped CdO [6]. The microstrain is higher for the sample prepared at low temperature and decreases as the temperature increases indicating that the broadening is due to grain size.

The lattice parameters were determined from the interplaner spacing equation and Bragg's law using the X-ray diffraction peaks. As seen from the table, the addition of Ag dopant caused no significant changes in the lattice parameters indicating that the introduction of Ag in CdO nanoparticles did not distort the structure.

### 3.2. UV-Vis spectroscopy

The UV-Vis absorption spectra of undoped CdO preheated at 400 °C as well as Ag-doped CdO at 400 and 500 °C are shown in figure 2. From the figure, one can observe the absorption excitonic peaks at  $\sim 557$  nm for undoped CdO and  $\sim 475$  nm and  $\sim 508$  nm for the Ag doped CdO samples heated at 400 and 500 °C, respectively. As can be seen from the UV-vis spectra, the excitonic peaks are very broad.

A similar behaviour was observed by J. Liu *et. al.* on pure CdO prepared using thermal decomposition reaction [6]. The corresponding band gap energies of absorption maximum for the samples were calculated using the following equation:

$$E = \frac{hc}{\lambda}$$

where  $E$  is the absorption band gap,  $h$  is the plank constant,  $C$  is a speed of light,  $\lambda$  = absorption excitonic peak wavelength.

The corresponding band gaps obtained were 2.23 eV for the undoped sample preheated at 400 °C and 2.61 eV and 2.44 eV for Ag-CdO preheated at 400 and 500 °C; respectively. The reported value [7] of the direct band gap of bulk CdO is 2.3 which is comparable to the present results.

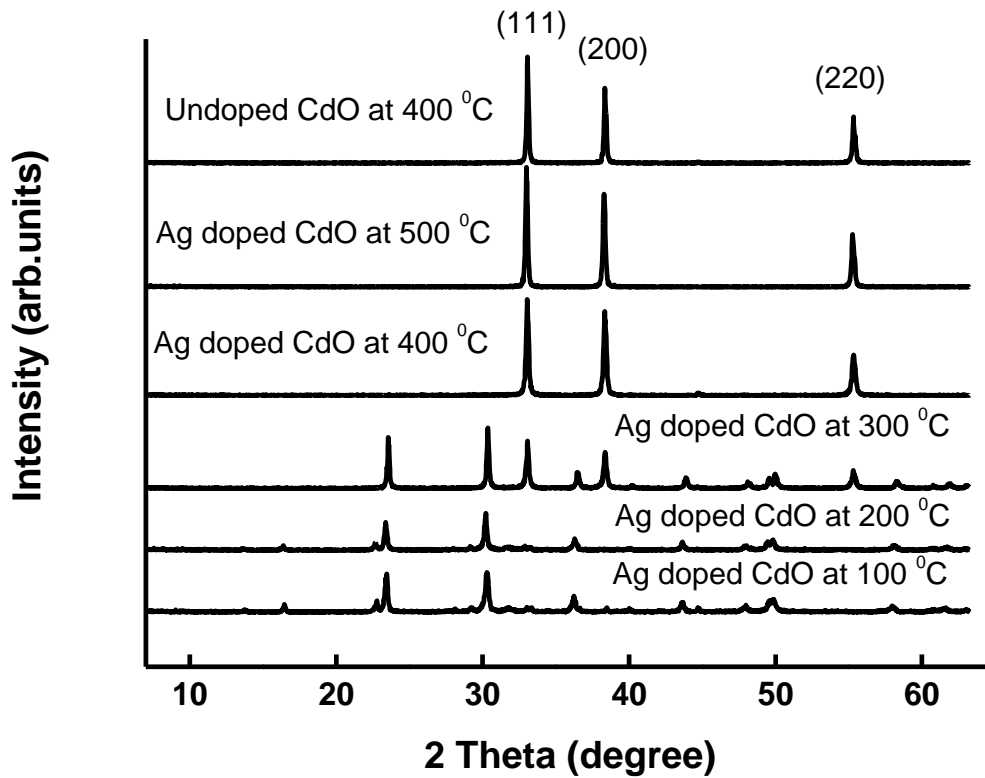


Figure 1. XRD patterns for undoped CdO annealed at 400 °C and 5% Ag doped CdO annealed at 100 °C, 200 °C, 300 °C, 400 °C and 500 °C.

Table 1. Average grain sizes (D), Lattice parameters, energy band gaps and strain ( $\epsilon$ )

Sample	Temperature °C	Lattice parameters		D (nm)	Band gap (eV) $\pm$ 0.03	E ( $\times 10^{-3}$ )
		a = b = c (Å)	Volume (Å) <sup>3</sup>			
Undoped CdO	400	4.690	103.182	51.19	2.23	1.948
5%Ag-CdO	400	4.691	103.228	40.03	2.61	2.490
5%Ag-CdO	500	4.699	103.757	47.03	2.44	2.108

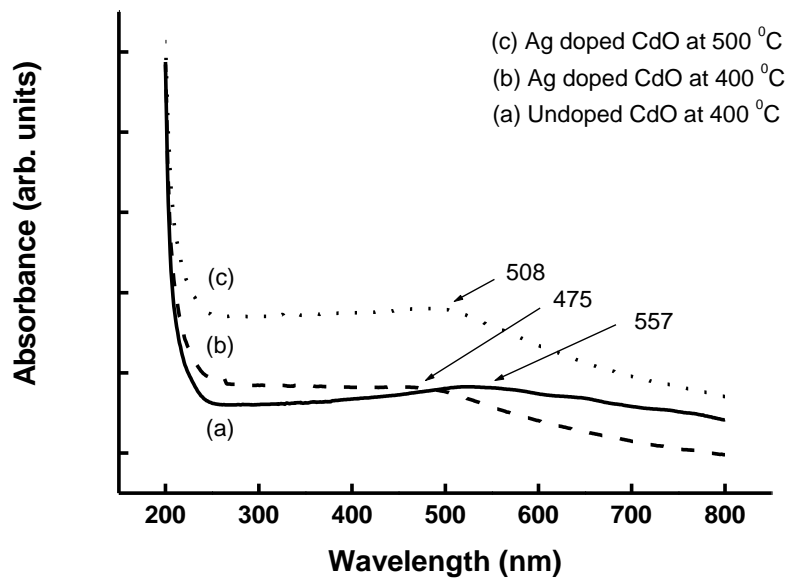


Figure 2. UV-Vis absorption spectra for Undoped CdO annealed at 400°C and 5% Ag doped CdO annealed at 400 °C and 500 °C.

The band gap of Ag doped CdO appears to have blue shifted from that of the undoped sample. This blue shift or band gap widening can be explained in terms of the Moss–Burstein (M–B) effect [8, 9]. According to this M-B theory, the optical absorption edge of a degenerate n-type semiconductor is shifted towards higher energy by the amount which is proportional to the free-electron density.

### 3.3. Photoluminescence

Previous reports have indicated that bulk CdO does not exhibit luminescence [10]. In the present work the photoluminescence (PL) of pure and Ag doped nanocrystalline CdO were detected. The PL emission spectra of the undoped sample preheated at 400 °C as well as those of Ag-doped CdO preheated at 400 and 500 °C are shown in figure 3. All the spectra were measured using an exciting wavelength of 325 nm. The PL spectra are dominated by the green emission peak around 410 nm. This is comparable to the result obtained for CdO film prepared by spray pyrolysis [11] in which the peak was found at 413 nm. This peak is ascribed to an exciton bound to a donor level. The PL intensity of Ag-doped CdO is higher than that of the undoped sample. Since the PL emission mainly results from the recombination of excited electrons and holes, the higher PL intensity indicates that an introduction of Ag increases the recombination rate. The intensity further increases as the annealing temperature increases.

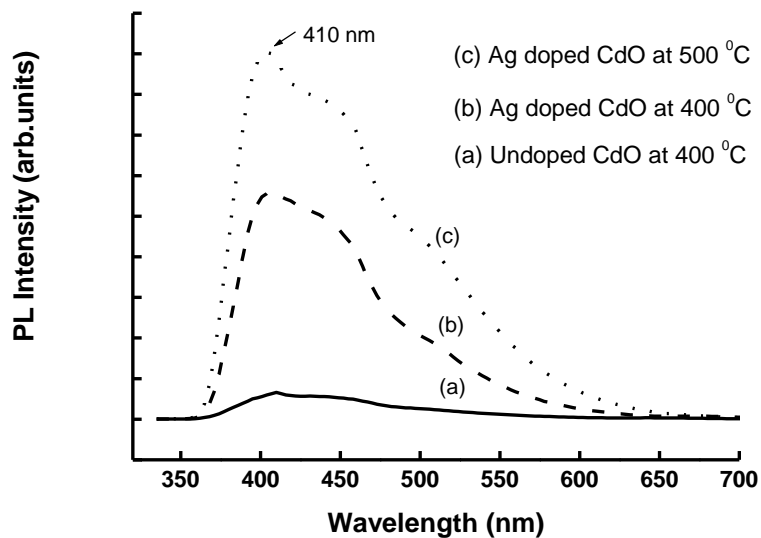


Figure 3. Photoluminescence spectra for Undoped CdO annealed at 400°C and 5% Ag doped CdO annealed at 400 °C and 500 °C.

### 3.4. SEM

The SEM micrographs are shown in figure 4. The morphologies of the powders are almost spherical in shape. The micrographs also reveal that the particles are agglomerated. Agglomeration could be due to strong hydrogen bonding in the gel network, which is then difficult to remove in the subsequent stages. At very high temperatures, the degree of crystallinity as well as agglomeration further increases considerably. The results are consistent with the XRD results in that as the temperature increases particle size increases and crystallinity improves as indicated by the broadening of the XRD peaks.

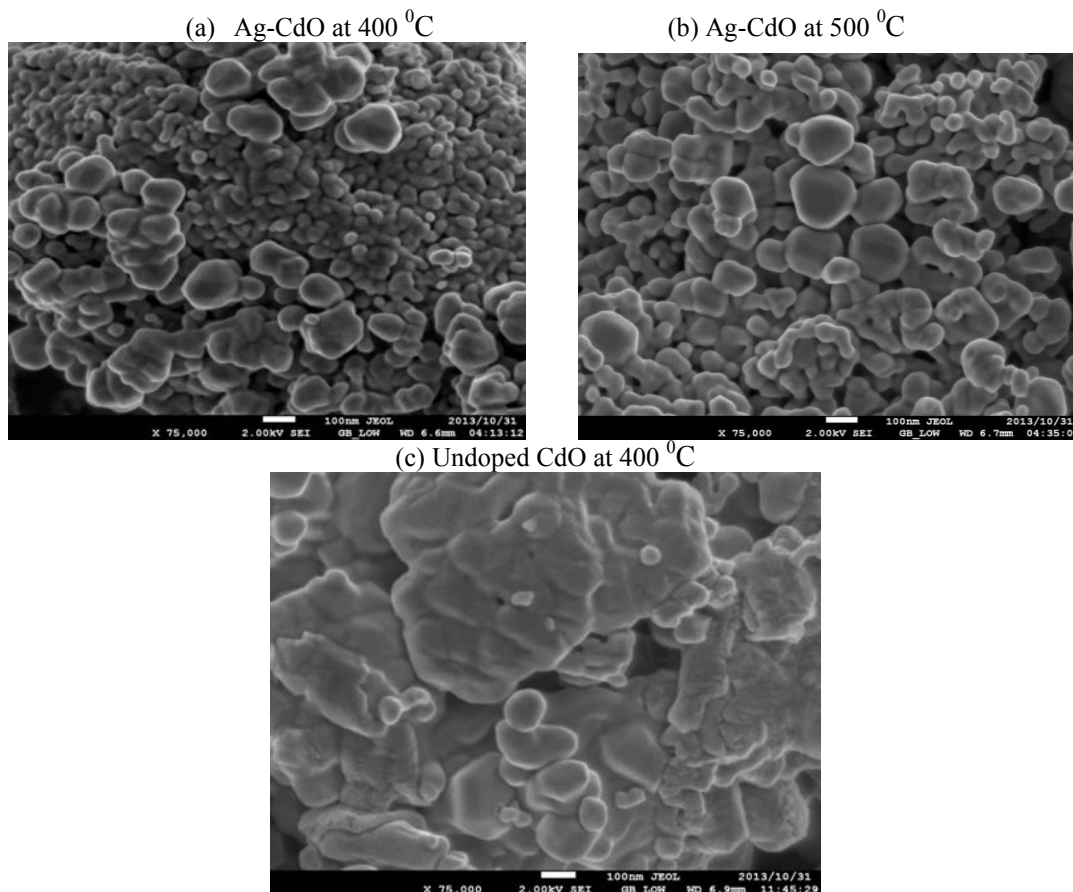


Figure 4. SEM micrographs of Ag-CdO (a) and (b) as well as the undoped CdO (c).

#### 4. Conclusion

XRD results revealed that both the undoped and 5% Ag doped CdO nanoparticle samples had a cubic crystalline structure (FCC structure). Introduction of Ag dopant in CdO had no significant effect on the lattice parameters of CdO nanoparticles. The strains decreased with an increase in annealing temperature indicating that peak broadening is due to grain size. The average grain sizes increased as the annealing temperature was increasing. The introduction of Ag in CdO resulted in the blue shifting of the band gap from that of the undoped sample. The PL intensity of Ag-doped CdO is higher than that of the undoped sample indicating that an introduction of Ag increases the recombination rate. The SEM results confirmed what is observed with XRD in that the average grain sizes of the samples increased with an increase in the annealing temperature.

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