

## Band gap narrowing of CdO powder by rare earth neodymium doping

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Rare earth Nd-doped CdO powders with various Nd contents (0-2.0 at.%) were synthesized by a coprecipitation process and characterized by X-ray diffraction, field emission scanning electron microscopy, and UV-vis spectrophotometry. The experimental results indicate that the Nd doping led to a decrease of the average particle size and a change of thenoptical property. The band gap of the CdO powder was suddenly narrowed about 12.45% due to a slight Nd doping of 0.5 at.% and then increased with further increasing Nd content. This variation was explained by the available band gap narrowing models.

Key words: CdO, Nd-doping, Semiconductor, Band gap, Optical properties.

### Introduction

Pure and metal doped degenerate semiconducting cadmium oxide (CdO) has been used in a wide range of optoelectronic applications such as a transparent conducting oxide, solar cells, smart windows, and optical communications, as well as other type of applications such as IR heat mirrors and gas sensors, etc. [1-5]. These applications are based on its (CdO) optical and electrical properties [1, 6-9], which may be controlled through doping with different types of metallic ions. It was observed that doping of CdO with some metallic ions of a smaller radius than that of Cd<sup>2+</sup>, such as In, Sn, Al, Sc, and Y, improved its electrical conduction properties, and increases its optical energy gap [1, 10-14]. However, Dakhel [15] studied the possibility of controlling the optoelectrical properties of CdO through doping with rare earth ions Sm<sup>3+</sup> because of its smaller ionic radius than that of Cd<sup>2+</sup> and found that Sm<sup>3+</sup> ions doping obviously narrowed the optical band gap and increased conductivity with a slight doping level of 0.4 at.%. He further found that Dy [15] and Ce [17] dopings had similar effects on the optoelectric properties of the CdO. Recently, the potential doping candidates of the rare earth oxides of Gd [18] and Li-Ni [19] gave an improvement of the optical and electrical properties of CdO films. The literature survey indicates that there is no report on optoelectrical properties of Nd-doped CdO materials. The aim of the present study was to investigate the effects of Nd doping as different levels on the structural and optical properties of CdO powders for the first time.

### Material and Methods

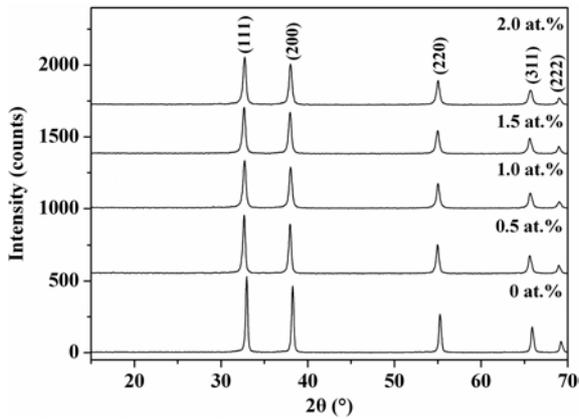
The starting materials used were all of analytical grade. For synthesis of the Nd-doped CdO powders, Nd(NO<sub>3</sub>)<sub>3</sub> and CdSO<sub>4</sub> powders were first dissolved in deionized water with constant stirring according to the designed Nd contents of 0, 0.5, 1.0, 1.5 and 2.0 at.%. Deionized water was added into the solutions to achieve a total metal cation concentration of 0.01 mole l<sup>-1</sup>. Subsequently, ammonia (36 wt. % NH<sub>3</sub>) was slowly dropped into the solutions with constant stirring until a solution pH ~ 10. In this process, white precipitates were rapidly formed in the solutions. After an aging of 1 h at room temperature, the solutions were filtrated and washed with an ammonia aqueous solution with a pH ~ 9-10 for several times. Finally, the precipitates were dried at 100 °C for 24 h and calcined at 400 °C for 2 h.

The structural phase of the Nd-doped CdO powders was identified at room temperature using an X-Ray diffractometer (XRD, CuK<sub>α1</sub>, λ = 0.15406 nm, Model No: D/Max-2200PC, Rigaku, Japan), and the morphology and size of the powders were analyzed using a field emission scanning electron microscope (EF-SEM, Model No: JXM-6700F, Japan). The diffuse reflectance absorption spectra of the powders were determined with UV-vis spectrophotometer (Model No: Lambda 950, Bruker Daltonics, USA).

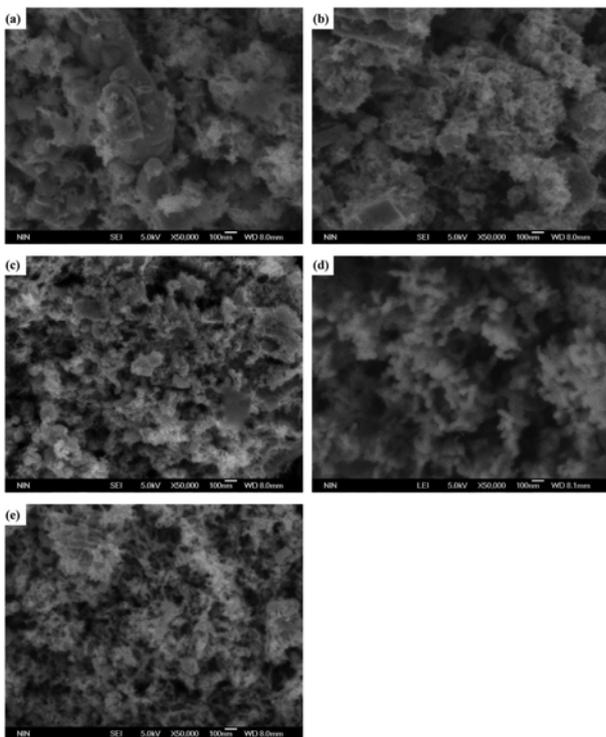
### Results and Discussion

Figure 1 shows the XRD patterns of the Nd-doped CdO powders. Montepionite CdO with a cubic structure was the only XRD detectable phase of the powders (PDF#76-0653). This might indicate that the Nd<sup>3+</sup> cations entered the CdO lattice by the cation doping. The powders demonstrate intensity ratios of I<sub>(200)</sub>/I<sub>(111)</sub> = 0.857-0.889. This implies that the powders are

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**Fig. 1.** XRD patterns of the CdO: Nd powders with different Nd contents.



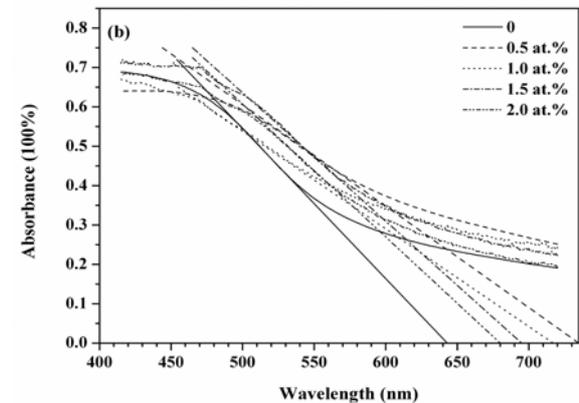
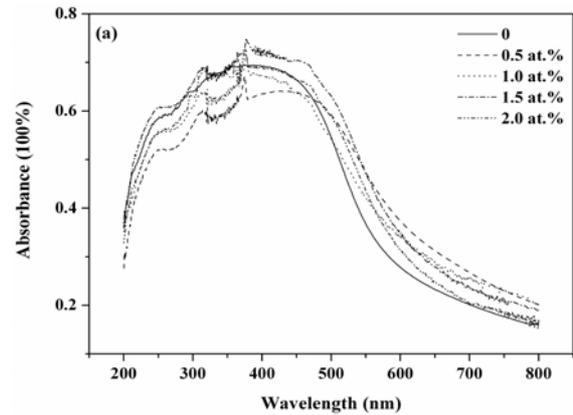
**Fig. 2.** SEM micrographs of the CdO: Nd powders with Nd<sup>3+</sup> contents of (a) 0 at.%, (b) 0.5 at.%, (c) 1.0 at.%, (d) 1.5 at.%, (e) 2.0 at.%.

of a weak *a*-orientation in comparison with the standard XRD intensity ratio of  $I_{(200)}/I_{(111)} = 0.858$ .

Monteponite CdO is a cubic crystalline phase, so the lattice parameters of the powders can be calculated with XRD data analysis by following equation:

$$\frac{a^2}{d^2} = h^2 + k^2 + l^2 \quad (1)$$

The calculated lattice parameter was  $a = 4.7233 \text{ \AA}$ ,  $4.7241 \text{ \AA}$ ,  $4.7244 \text{ \AA}$ ,  $4.7249 \text{ \AA}$ , and  $4.7251 \text{ \AA}$  for the powders with Nd contents of 0 at.%, 0.5 at.%, 1.0 at.%, 1.5 at.%, and 2.0 at.%, respectively. The *a* value of the doped powders were overall slightly larger than that of the pure CdO powder and increased with an increase in



**Fig. 3.** (a) UV-vis. absorption spectra of the CdO: Nd powders and (b) enlarged figures in wavelength range of 425-710 nm.

the Nd content due to larger ionic radius ( $1.03 \text{ \AA}$ ) of Nd<sup>3+</sup> cation than the Cd<sup>2+</sup> cation ( $0.97 \text{ \AA}$ ).

Figure 2 shows FESEM micrographs of the Nd-doped CdO powders. The powders demonstrated granular particle morphologies, and the average particle size was in the range of  $\sim 25$ - $210 \text{ nm}$  which almost decreased as increase in the Nd content.

Figure 3 shows the absorption spectra of the Nd-doped CdO powders with various Nd contents. The absorbance in the UV-visible range first increased and then decreased with increasing Nd content. The maximum absorbance appeared at Nd contents of 0.5-1.0 at. %. From Fig. 3b, the light absorption first red-shifted and then blue-shifted with increasing Nd content. The absorption edge of powders increased from  $643 \text{ nm}$ , to  $735 \text{ nm}$ , and decreased to  $717 \text{ nm}$ ,  $695 \text{ nm}$  and  $680 \text{ nm}$  with an increase in the Nd content. Accordingly, the band gap ( $E_g$ ) decreased from  $1.929 \text{ eV}$  to  $1.687 \text{ eV}$  with increasing Nd content from 0 to 0.5 at.% and then increased to  $1.729 \text{ eV}$ ,  $1.784 \text{ eV}$ ,  $1.8254 \text{ eV}$  at Nd contents of 1.0 at.%, 1.5 at.%, and 2.0 at.%, as shown in Fig. 4. For pure CdO, the band gap obtained was smaller than that ( $2.2$ - $3.0 \text{ eV}$ ) of the films prepared by different techniques [1, 15-21]. The band gap of the host CdO suffers from a sudden decrease by about 12.5% due to the slight Nd<sup>3+</sup> doping of 0.5 at.%. In general, rare earth cation doping results

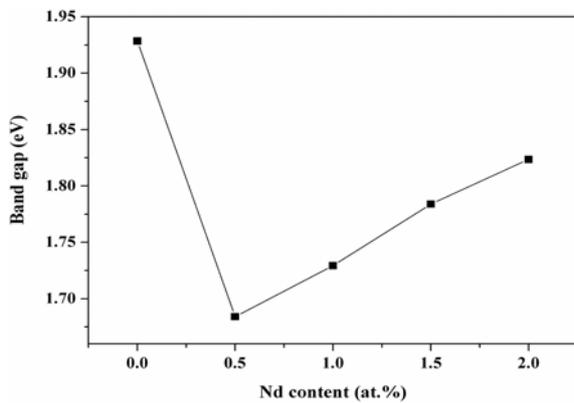


Fig. 4. Variation of the band gap energy with Nd content.

in an increase of the carrier concentration of a semiconductor such as CdO and hence the band gap widening on the Moss-Burstein effect [20, 21]. Such a decrease of  $E_g$  is contradictory to the usually expected Moss-Burstein effect. This sudden decrease can be explained by the change in the nature and strength of the crystalline potential by adding the influence of  $\text{Nd}^{3+}$  ions and the effect of their 4f-electrons on the crystalline electronic energy spectrum. Due to the light doping, the band tailing or impurity band becomes broader and finally reaches and merges with the bottom of the conduction band causing the sudden decrease of the optical band gap. The relative gradual variation of  $E_g$  among rare earth ion-doped samples was investigated in the present study through the available models that related the change of  $E_g$  to the change of carrier concentration [15-17]. The increase of the carrier concentration in degenerate semiconductors causes theoretically two opposite effects, namely the band gap widening and band gap narrowing (BGN). The BGN could play the major role in an explanation of the present results due to the high density of carriers. The BGN consists of two parts [15-17]. The first part comes from the electron-impurity interaction. The second part of BGN arises from the coulombic interaction between the carriers and results in the band gap shift [22]. In addition, Gupta et al. [19] also related the possible reason for the decrease in optical bandgap of Li-Ni co-doped CdO thin films to the change in the grain size of the films.

## Conclusions

Nd-doped CdO powders with Nd contents of 0-2.0 at.% have been synthesized by a coprecipitation method. Nd cations was completed entered the CdO lattice in the studied range of Nd content. The Nd doping significantly affected the absorbance and the band gap energy of the powders. With increasing Nd content, the average particle size decreased, the absorbance of the powders in the range of UV-visible light decreased and then enhanced, and the band gap was narrowed and then returned. A maximum  $E_g$

decreased about 12.5% was obtained due to the slight  $\text{Nd}^{3+}$  doping of 0.5 at.%. This may be of significance to the optical application of CdO: Nd materials.

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