# Sol–gel synthesis, characterization, and optical properties of Gd<sup>3+</sup>-doped CdO sub-micron materials

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## Abstract

Highly crystalline  $Gd^{3+}$ -doped cadmium oxide micro-structure was synthesized by calcining the obtained precursor of a sol-gel reaction. The reaction was carried out with cadmium nitrate (Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O), gadolinium oxide, and ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) reactants without any additives at 80°C for 2 h. The resulting gel was calcined at 900°C with increasing temperature rate of 15°C/min for 12 h in a furnace. As a result of heating, the organic section of the gel was removed, and the  $Gd^{3+}$ -doped cadmium oxide micro-structure was produced. The obtained compound from the sol–gel technique possesses a cubic crystalline structure at a micro scale. XRD study indicates that the obtained  $Gd^{3+}$ -doped CdO has a cubic phase. Also, the SEM images showed that the resulting material is composed of particles with cluster structure. Also, FT-IR spectroscopy was employed to characterize the  $Gd^{3+}$ -doped CdO micro-structures.

# Keywords

Sol-gel method, Cadmium oxide, Gadolinium, PXRD patterns

# Background

Recent research on luminescent nanomaterials provides challenges to both fundamental and breakthrough development of technologies in various areas such as electronics, photonics, display, lasing, detection, optical amplification, and fluorescent sensing in biomedical engineering and environmental control [1]. Gadolinium oxide  $(Gd_2O_3)$  has been frequently used as host material due to abundant resource in nature. Further, Gd is a known contrast agent for magnetic resonance imaging (MRI), and thus the rare-earth ion-doped Gd<sub>2</sub>O<sub>3</sub> can be used in dual, MRI, and fluorescence imaging applications [2] and as a drug carrier [3]. In addition, pure and doped Gd<sub>2</sub>O<sub>3</sub> films have been studied as high dielectric constant gate dielectric films, phosphor films, and scintillating films [4,5]. The films of transparent conductive oxides (TCO) such as cadmium oxide (CdO) have been extensively studied because of their use in semiconductor optoelectronic device technology [6]. Among the TCO, CdO films have been successfully used for many applications, including use in gas-sensing devices, photodiodes, transparent electrodes, phototransistors, and photovoltaic solar cells [7]. Also, CdO is an n-type semiconductor with a cubic crystal structure, possesses a direct band gap of 2.2 eV [8]. Besides, CdO shows very high electrical conductivity even without doping due to the existence of shallow donors caused by intrinsic interstitial cadmium atoms and oxygen vacancies [9]. In previous studies, the synthesis of Sn-doped CdO thin films [10], Bi<sup>3+</sup>-doped CdO thin films by sol-gel spin coating method [11], copper-doped CdO nanostructures [12], ZnO-doped CdO materials [13], titanium-doped CdO thin films [14], ZnO-CdO-TeO<sub>2</sub> system doped with the Tb<sup>3+</sup> and Yb<sup>3+</sup> ions [15], N-doped CdO [16], samarium-, cerium-, europium-, Fe-, and Li-doped CdO nanocrystalline materials [17-21], Indoped CdO films [22], fluorine-doped CdO [23], gallium-doped CdO thin films [24], Gddoped CdO thin films with different method, dopant amount and structural morphology [25], Li-Ni co-doped CdO thin films [18], aluminum-doped CdO thin films [26], fluorine-doped CdO Films [27] have been reported.

In this work, crystalline  $Gd^{3+}$ -doped CdO micro-size layer has been synthesized by sol–gel method, with cadmium nitrate (Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O), Gd<sub>2</sub>O<sub>3</sub>, and ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) as raw materials without using any catalyst or template at a heat treatment temperature of 900°C with increasing temperature rate of 15°C/min for 12 h, which is a very simple and economical method. Also, we discuss about dopant-concentration effect on the morphology of the synthesized materials. The product was characterized by XRD, SEM, and FT-IR techniques.

## Methods

All chemicals were of analytical grade, obtained from commercial sources, and used without further purification. Phase identifications were performed on a powder X-ray diffractometer D5000 (Siemens AG, Munich, Germany) using CuK $\alpha$  radiation. The morphology of the obtained materials was examined with a XL30 scanning electron microscope (Philips, Amsterdam, Netherlands). Also, FT-IR spectra were recorded on a Tensor 27 (Bruker Corporation, Germany).

#### Synthesis of $Gd_xCd_{1-x}O$ sub-micron layer (x = 0.02, 0.04, 0.08, and 0.1%)

 $Cd(NO_3)_2 \cdot 4H_2O$  with molar concentrations of 4.83, 4.73, 4.68, and 4.63 mmolar (Mw = 308.482 g mole<sup>-1</sup>),  $Gd_2O_3$  with molecular concentrations of 0.049, 0.098, 0.0195, and 0.244 mmolar (Mw = 362.5 g mole<sup>-1</sup>), and 10 ml  $C_2H_6O_2$  were added into 400 ml distilled water. Then, the solution was stirred at 80°C for 2 h until a dried gel was obtained. The gel was brown color and spongy. The dried obtained gel was treated thermally at 900°C for 12 h. After the reaction was completed and cooled slowly to room temperature, the obtained material was pulverized. The sample was a black-colored powder.

### **Results and discussion**

#### **Powder XRD analysis**

In order to investigate the structural properties of Gd<sup>3+</sup>-doped CdO micro-structures, X-ray diffraction measurements varying the diffraction angle (with 3° interval) from 4° to 70° were performed. The Gd<sup>3+</sup>-doped CdO diffraction peaks at  $2\theta$  values of 33.10°, 38.39°, 55.32°, 65.96°, and 69.31° at x = 0.08 mmole compared to  $2\theta$  values of 32.97°, 38.27°, 55.25°, 65.86°, and 69.21° corresponded to pure CdO matching with the 111, 200, 220, 311, and 222 of cubic CdO (JCPDS-05-0640), indicating the formation of CdO- and Gd<sup>3+</sup>-doped CdO with excellent crystallinity. Figure 1 represents the powder XRD (PXRD) patterns of the obtained material after the 12-h reaction time at 900°C and at  $x_{Gd} = 0.02, 0.04, 0.08, and 0.1$  mmole, respectively. Figure 1 spectrum d shows that increasing the dopant amount to  $x_{Gd3+} = 1$  mmol, the diffraction peaks at  $2\theta$  values of  $29^\circ$ ,  $47^\circ$ , and  $57^\circ$  match with 222, 440, and 622 assigned to cubic Gd<sub>2</sub>O<sub>3</sub> [1-3]. So, the doping limitation is x = 0 to 0.08 mmole. Crystal sizes were measured via Debye-Scherrer's equations, which are as follows: 29.0, 27.8, and 27.65 nm for x = 0.02, 0.04, and 0.08 mmole dopant concentration, respectively. Also, the interplanar spacing in the crystalline material is calculated via Bragg's law ( $n\lambda = 2d_{hkl} \sin \theta$ ) selecting the peaks h, k, and l at 200. The radius of  $\text{Gd}^{3+}$  (r = 0.94 Å [28]) is smaller than the radius of  $Cd^{2+}$  (r = 1.1 [28] Å); compared to those of the pure particles, the diffraction lines in the powder XRD patterns of  $Gd^{3+}$ -doped CdO shift to higher  $2\theta$  in doped CdO. So, we have the following equations:  $\Delta 2\theta = 38.39$  (doped) - 38.27 (pure)  $= 0.12^{\circ}$  and  $\Delta d = 2.34903$  (pure) -2.34196 (doped) = 0.00707 Å. The shift in the diffraction lines might be attributed to the smaller radius of the dopant ion, compared to the ionic radius of the  $Cd^{2+}$ , which may cause a contraction of the unit cell and so decrease the lattice parameters in the Gd<sup>3+</sup>-doped CdO materials. The pattern shows the polycrystalline of cubic CdO structure (NaCl structure of a space group Fm3m). According to JCPDS-05-0640, the lattice constants for an undoped CdO sample were a = 0.46950 nm. Also, we used CelRef software version 3, using XRD patterns  $2\theta$  and h, k, and l values, to refine the cell parameters. Pure CdO cell parameters calculated as a = 0.46941 nm and for doped CdO (in x = 0.08 mmole) were a = 0.46912 nm. The calculations showed that the unit cell volume of pure CdO is  $0.1034 \text{ nm}^3$  and that of the doped CdO is  $0.10324 \text{ nm}^3$ . So, we can conclude that there is a contraction in the unit cell when doping Gd<sup>3+</sup> in CdO. The PXRD measurements confirm that a pure phase of the cubic CdO is formed [28-34].

Figure 1 PXRD patterns of the synthesized pure CdO and  $Gd_xCd_{1-x}O$  micro-material. (a) Pure CdO, (b) x = 0.02, (c) x = 0.04, (d) x = 0.08, and (e) x = 0.1 mmole.

#### Micro-structure analysis

Figure 2 reveals the SEM images of the cubic structure of the obtained crystalline CdO at 900°C [33]. Remarkably, it was observed that the average particle size is 2 µm. As shown in Figure 2a,b, it is clear that the material is composed of particles with heterogeneous size. Figure 2c shows that the sample is nearly a layer-like structure with macro-pores which resulted from the calcination treatment. Figure 2d,e shows that the morphology is clearly like a layer, with the particle almost spherical in shape and size in a range of about 2 to 3 µm. SEM images in Figures 3, 4, and 5 reveal the general morphological aspect of the powder particles. SEM images of the synthesized Gd<sup>3+</sup>-doped CdO sub-micron materials are presented in Figure 3, 4, and 5. Figure 3 shows the SEM images of Gd<sub>0.02</sub>Cd<sub>0.98</sub>O sub-micron particle. The synthesis of the sol-gel system led to the formation of spheroidal-shaped particle clusters. As shown in Figure 3a,b, with low magnification, the sample is like a macro-porous structure, and it is clear that the particle sizes that formed the structure are heterogonous. With high magnification, this figure shows that there are small particles (uncus) on the surface of the particles. The average uncus particle size was estimated between 200 and 300 nm. With higher magnification, Figure 3c,d shows that the multigonal particle sizes are about 1 µm. Compared to pure CdO, it seems that the morphology of the particles is changed from layer-like to macro-porous particles. Figure 4a,b shows Gd<sub>0.04</sub>Cd<sub>0.96</sub>O; due to increasing dopant concentration, the number of uncus particles is increased. The uncus sizes are a little smaller than those of  $Gd_{0.02}Cd_{0.98}O$  sub-micron particle. In Figure 4c,d, it is clear that with increasing dopant concentration, the morphology of the synthesized materials is almost unchanged. Figure 5a,b shows Gd<sub>0.08</sub>Cd<sub>0.92</sub>O; due to increasing dopant concentration, the morphology of the particles was changed to a layer-like structure. Also, in Figure 5c,d, it is clear that there are particles with spheroid structure. The particle sizes are heterogeneous and about 1  $\mu$ m. In Figure 5d, it is clear that the width of the layer structure is about 3  $\mu$ m. This Figure shows that there are small particles on the surface of the layer as uncus. The uncus particle sizes are heterogeneous and are estimated to be between 100 and 500 nm; considering the smallest uncus particle (100 nm), the uncus particles in Figure 5 are smaller than those of  $Gd_{0.04}Cd_{0.96}O$ .

Figure 2 The SEM images of the synthesized CdO sub-micron materials.

Figure 3 The SEM images of the synthesized Gd<sub>0.02</sub>Cd<sub>0.98</sub>O sub-micron materials.

Figure 4 The SEM images of the synthesized Gd<sub>0.04</sub>Cd<sub>0.96</sub>O sub-micron materials.

Figure 5 The SEM images of the synthesized Gd<sub>0.08</sub>Cd<sub>0.92</sub>O sub-micron materials.

#### Spectroscopic study

Figure 6 shows the FT-IR spectrum diagram of the doped samples. The bands around 3,460 and 1,650 cm<sup>-1</sup> are due to the OH stretching vibration and OH deformation vibration, respectively. The absorption appearing around 1,510 and 1,410 cm<sup>-1</sup> corresponds to CO asymmetric vibration. The band at 540 cm<sup>-1</sup> is assigned to the Gd-O vibration mode of the cubic Gd<sub>2</sub>O<sub>3</sub> [3]. Also, we know that the peaks at 800 to 1,400 are assigned to CdO [35]. Peak at 1,541 cm<sup>-1</sup> corresponded to the residual organic components [36].

Figure 6 FT-IR spectra of the synthesized  $Gd_xCd_{1-x}O$  sub-micron materials. (a) x = 0.02, (b) x = 0.04, (c) x = 0.08 mmole obtained after 12 h at 900°C.

## Conclusion

In summary, micro-layers of  $\text{Gd}^{3+}$ -doped CdO were synthesized successfully by employing a simple sol–gel method. We found that the dopant concentration affects the morphology of the final product. As shown by the SEM images, with increasing dopant concentration, the morphology of the cluster-like micro-crystals changed to partially layered structures. We found that compared to those of the micro-size material of pure CdO, the diffraction lines in the powder XRD patterns of  $\text{Gd}^{3+}$ -doped CdO shifted to higher  $2\theta$  values. The shift in the diffraction lines might be attributed to the smaller radius of the dopant ion, compared to the ionic radius of the Cd<sup>2+</sup>, which may cause a contraction of the unit cell and so decrease the lattice parameters in the Gd<sup>3+</sup>-doped CdO materials. These materials are expected to have a potential application in dual, MRI, and fluorescence imaging applications and as a drug carrier.

# **Competing interest**

The authors declare that they have no competing interests.

# **Authors' contributions**

All authors (AA, SK, SWJ, MD, AB, HM, and SS) participated in the experiments and read and approved the final manuscript.

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