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Sol Sol-gel synthesis, structural and optical properties investigation of Ce^{4+} doped CdO sub-micron materials

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Abstract

Highly crystalline Ce^{4+}-doped cadmium oxide sub-micron structures were synthesized by calcinations of the obtained precursor of a sol-gel reaction. The reaction was carried out with cadmium nitrate ($Cd(NO_3)_2.4H_2O$), cerium nitrate $Ce(NO_3)_4.6H_2O$ and ethylene glycol ($C_2H_6O_2$) reactants without any additive at 80°C for 2h. Resulting gel was calcined at 900 °C with increasing temperature rate of 15°C per minute for 12 h in a furnace. As a result of heating, the organic section of the gel was removed and Ce^{4+}-doped cadmium oxide micro structure was produced. The obtained material synthesized from the sol-gel technique, possesses a cubic crystalline structure at micro scale. X-ray diffraction (XRD) study indicates that the obtained Ce^{4+}-doped CdO has a cubic phase. SEM images showed that the resulting material is composed of particles with cluster structure. Other two techniques FT-IR and UV-Vis spectroscopies were employed for further characterization of the Ce^{4+}-doped CdO micro structures.

Keywords: Sol-Gel Method, Cadmium Oxide, Cerium, micro structures, XRD patterns.

1. Introduction

Ceria and the oxide materials containing ceria have attracted much attention as oxidation catalysts for their high activity in the redox reactions and high oxygen storage capacity. The redox properties and the lattice oxygen mobility of CeO_2 can be profoundly enhanced when used in combination with other metal oxides [1]. Also, CeO_2 based compounds exhibit poor mechanical stability [2]. Materials based on cerium oxide have been extensively used as glass polishing materials oxygen ion conductor in solid oxide fuel cells (SOFCs), gas sensors, UV absorbent and catalytic supports or promoter for automotive exhaust gas conversion reaction. The fine powder of cerium oxide has suitable features for use in personal care products based on inorganic materials for blocking of ultraviolet radiation [3]. Also ceria manifests a lower photocatalytic activity than that of zinc and titanium oxides but it still has an important catalytic behavior for oxidation of organic compound limiting its commercial use. Additionally, it also slightly absorbs in the visible range producing a yellowish coloring in the products, mostly undesired in specific applications [4]. For these reasons we chose CeO_2 as dopant agent. The films of transparent conductive oxides (TCO) such as zinc oxide, indium-tin oxide, tin oxide and cadmium oxide (CdO) have been extensively studied because of their use in semiconductor optoelectronic device technology [5]. Among these TCO, CdO films have been successfully used for many applications, including use in gas sensor devices, photo diodes, transparent electrodes, photo transistors, and photovoltaic solar cells [6]. CdO is an n-type semiconductor with a Cubic crystal structure,

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possesses a direct band gap of 2.2 eV [7]. Beside, 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 [8]. In previous studies, synthesis of Sn-doped CdO thin films [9], Bi^{3+}-doped CdO thin films by sol–gel spin coating method [10], Cu doped CdO nanostructures [11], ZnO doped CdO materials [12], Ti-doped CdO thin films [13], ZnO–CdO–TeO_2 system doped with the $Tb^{3+}$and Yb^{3+} ions [15], N-doped CdO [16], Sm, Ce, Eu, Fe and Li-doped CdO nanocrystalline materials [13, 17 - 21,], In doped CdO films [20], Ga doped CdO thin films [22], Gd doped CdO thin films [23], Li–Ni co-doped CdO thin films [24], Al-doped CdO thin films [25], F-doped CdO Films have been reported [26]. Also, the authors have reported the synthesis of Gd^{3+} doped CdO via this experimental sol-gel method [27].

In this work, crystalline Ce^{4+} doped CdO micro-size layer has been synthesized by sol-gel method. The raw materials are cadmium nitrate, cerium nitrate $Ce(NO_3)_4.6H_2O$ and ethylene glycol ($C_2H_6O_2$) without using any catalyst or template. The heat treatment temperature was 900 °C with increasing temperature rate of 15°C per minute for 12h reaction time. This method is a very simple and economical method. In addition, the dopant concentration effect on the morphology of the synthesized materials would be discussed. The products were characterized by XRD, FE-SEM, UV-Vis FT-IR techniques.

2. Experimental

2.1. Apparatus

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 Siemens D5000 using Cu Kα radiation (λ=1.542Å). The morphology of the obtained materials was examined with a Philips XL30 Scanning Electron Microscope. Absorption spectra were recorded on a Jena Analytik Specord 40. FT-IR spectra were recorded on a Tensor 27 Bruker. Also, cell parameter refinement was calculated by using cellref software version 3.

3. Synthesis of CdO micro size powder

Recently we have reported the synthesis of CdO sub-micron materials via sol gel method.

3.1. Synthesis of $Ce_xCd_{1-x}O$ sub-micron layer (x=0.5, 1 and 1.2 mmole)

4.853 mmolar, 4.829 mmolar and 4.819 (Mw=308.482 $g.mole^{-1}$) cadmium nitrate ($Cd(NO_3)_2.4H_2O$), 0.024 mmolar, 0.049 and0.0585 mmolar (Mw=434.222 $g.mole^{-1}$) cerium nitrate ($Ce(NO_3)_4.6H_2O$), respectively, and glycol ethylene ($C_2H_6O_2$) 10 ml were added to 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 and spongy. The dried obtained gel was treated thermally at 900 °C for 12 h with increasing thermal rate of 15° per minute. After the reaction completed, and cooled slowly to room temperature, the obtained material was pulverized. The sample was black like powder, macroscopically.

4. Results and discussion

4.1. XRD analysis

Phase identifications were performed on a powder X-Ray diffractometer Siemens D5000 using Cu Kα radiation (λ=1.542Å). Figure 1 shows polycrystalline of cubic CdO structure (NaCl structure of a space group Fm3m). In order to investigate the structural properties of Ce^{4+}-doped CdO micro structures X-ray diffraction measurement varying the diffraction angle, ϴ from 4◦ to 70◦ was performed. The Ce^{4+}-doped CdO diffraction peaks corresponded to pure CdO matching with that of cubic CdO (JCPDS-05-0640) indicated the formation of Ce^{4+} doped CdO with excellent crystallinity. Figure 1 represents the PXRD patterns of the obtained material after 12 h reaction time at 900°C and at $x_{Ce^{4+}}$=0.5, 1 and 1.2 mmole, respectively. Figure 1(c) shows that with increasing the dopant amount to $x_{Ce^{4+}}$=1.2 mmole, there are peaks at about $2\Theta\approx27$, 47, 57, 60° matching with the *h k l* 111, 220, 311, 222 assigned to cubic CeO_2 [1, 2, 3]. So the doping limitation is x=0-1 mmole. Interplanar spacing (d) in the crystalline material was calculated via Bragg's law ($n\lambda = 2d_{hkl} \sin \theta$), where n is called the order of reflection (we used n=1), d is interplanar spacing, ϴ is the half of diffraction angle and λ is the incident X-rays of wavelength, with selecting the peaks at *h k l*, 200. Because the radii of Ce^{4+} (r= 0.97 Å [3]) is smaller than the radii of Cd^{2+} (r=1.55 Å), so compared to those of the pure particles, the diffraction lines in the powder XRD patterns of Ce^{4+}- doped CdO, there is a shift to higher 2 theta so (Δ2θ=38.37 *(doped)* – 38.27*(pure)* =0.10°), (Δd=2.7135 (pure) - 2.7100 (doped) =0.0035Å). Because CeO_2 and CdO have cubic crystal phase, so they are iso-crystal phase. And because the radius of Ce is smaller than that of Cd when Ce is coming into CdO unit cell in the place of Cd, there is a contraction in the CdO unit cell. So we can conclude that as a result of the contraction, crystal size and inter planar spacing will be reduced. Table 1 shows XRD data for the obtained materials synthesized via the sol-gel method. According to the data mentioned in table 1, the diffraction angle (2ϴ) in the standard CdO compared to those of the pure synthesized CdO, shows a red shift in *d* showing an expansion of the synthesized CdO compared with the standard CdO. However, compared to the data for Ce doped CdO, with highest amount of Ce, there is a contraction in the unit cell compared to the pure CdO and standard unit cell structure. Also, crystal sizes of the obtained materials were measured via Debye Scherer's equation t=kλ/Bcosϴ, where *t* is entire thickness of the crystalline sample, $B_{1/2}$ of FWHM is the full width at half its maximum intensity and Θ_B is the half diffraction angle at which the peak location is, that are as follows: 28.27 and 26 nm, for x=0.5 and 1 mmole, and 29.2 nm for pure CdO, respectively. For this purpose, we collected the data information including2ϴ, ϴ, $B_{1/2}$ (degree), $B_{1/2}$ (radian), $\cos\Theta_B$ and crystal size for the peak with highest intensity at *h k l* 111, in table 2 to use Debye Scherrer equation. According to table 2, we found that 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 2ϴ and *h k l* values, to refine the cell parameters. Calculated cell parameters for pure CdO is a=0.46941 nm which is almost identical with those values given in Subramanyam et al. (1998) and Reddy et al. (1998). Calculated cell parameters for doped CdO, in x=1 mmole is a=0.46923 nm. The calculations showed that the unit cell volume for pure CdO is 0.1034 nm^3 and for doped CdO is 0.10331 nm^3. So we can conclude that there is a contraction in unit cell with doping Ce^{4+} in CdO. The XRD_measurements confirm that a pure phase of the Cubic CdO was formed [28- 32].

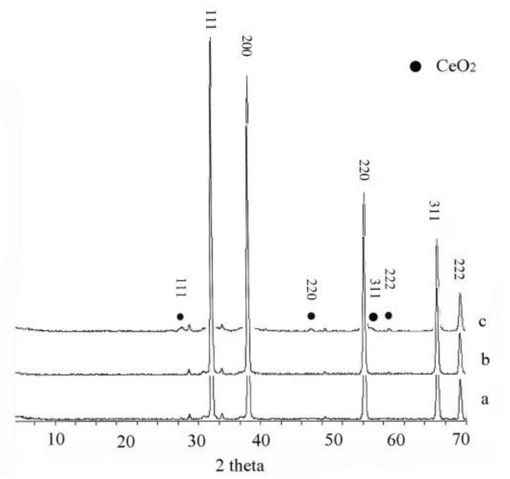

Figure 1. XRD patterns of the synthesized $Cd_{1-x}Ce_xO$ submicron size materials, where a is x = 0.5; b is x = 1; and c is x = 1.2 mole%.

Table 1. XRD data for pure, Ce-doped and standard value CdO submicron materials.

Ce doped CdO (x=1 mmole)				Pure CdO				Standard values			
h	*k*	*l*	*2ϴ*	*h*	*k*	*l*	*2ϴ*	*h*	*k*	*l*	*2ϴ*
1	1	1	33.1000	1	1	1	32.9900	1	1	1	33.0000
2	0	0	38.3700	2	0	0	38.2700	2	0	0	38.2830
2	2	0	55.3300	2	2	0	55.2500	2	2	0	55.2560
3	1	1	65.9800	3	1	1	65.8600	3	1	1	65.9080
2	2	2	69.2900	2	2	2	69.2100	2	2	2	69.2840

Table 2. Debye Scherrer data information for pure and Ce-doped CdO submicron materials.

Data information	2ϴ	ϴ	$B_{1/2}$(degree)	$B_{1/2}$(radian)	$\cos\Theta_B$	Crystal size (nm)
Pure CdO	32.99	16.495	0.28416	0.004957	0.95884	29.20
Ce doped CdO (x=0.5 mmole)	33.03	16.515	0.29350	0.005120	0.95874	28.27
Ce doped CdO (x=1 mmole)	33.10	16.550	0.31918	0.005568	0.95857	26.00

Micro structure analysis

The morphology of the obtained materials was examined with a Philips XL30 Scanning Electron Microscope. The FESEM images of the synthesized Ce^{4+}-doped CdO sub-micron materials are given in Figures 2 and 3. The SEM images in figure 2 reveal the general morphological aspect of the powder particles. Figure 2 shows SEM images of $Ce_{0.005}Cd_{0.995}O$ sub-micron material. The synthesis of the sol–gel system led to the formation of particles clusters of spherical shape. As shown in figures 2a and b, with low magnification, the sample is macro porous like structure and the average particle size was estimated about 800 nm-1 µm. The Figure shows that there are small particles on the surface of the particles as uncus. With higher magnification, figure 2c and d show that the uncus sizes are about 100 - 150 nm. It is observed from Figure 3 (a and b) that the number of uncus particles are increased with increasing the dopant concentration and the particle sizes are in about 700nm - 1µm that are smaller than those of mentioned in figure 2. The uncus sizes are about 80 - 100 nm. In figures 3c and d it is clear that particle sizes are almost identical. Also, it’s clear that with increasing the dopant concentration, the morphology of the synthesized materials is changed to almost layer like structure. Also, the particles have not compacted tightly in 0.05 mole% and with increasing the dopant amount, the porosity has decreased and layer structures are formed.

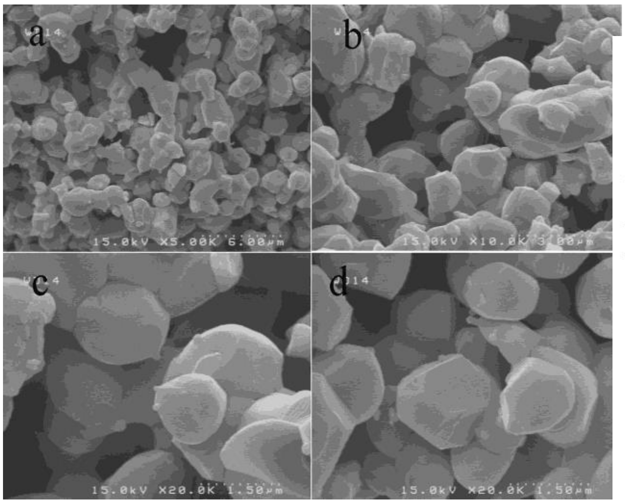

Figure 2. The SEM images of the synthesized $Cd_{0.995}Ce_{0.005}O$ micro size layer.

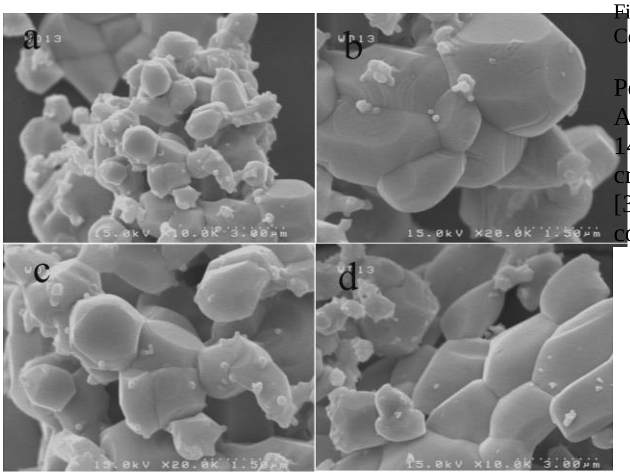

Figure 3. The SEM images of the synthesized $Cd_{0.99}Ce_{0.01}O$ micro size layer.

4.2. Spectroscopic studies

Absorption spectra were recorded on a Jena Analytik Specord 40. The electronic absorption spectra of the synthesized Ce^{4+} -doped CdO sub-micron materials are given in Figure 4. According to the spectrum, the CeO_2 presents the photoabsorption properties from UV light region to visible light shorter than 450 nm. So in figure 4a in x=0.05 mole%, there is a weak shoulder in about 285 nm corresponding to Ce^{4+} [35] that is behind the CdO band, a shoulder at 560 nm (E_{gap}=2.2 eV) corresponded to CdO [7] and a weak peak at 1050 nm that is corresponding to CdO [29, 31, 32]. With increasing the dopant amount to 1 mole%, a broad band is formed at 285 nm (E_{gap}=4.35 eV), that is corresponding to Ce^{4+} [33 - 35].

FT-IR spectra were recorded on a Tensor 27 Bruker. Figure 5 shows FT-IR spectrum diagram of the doped samples. From the present spectrum, the peak at 3419 cm^{-1} is corresponded to stretching vibration of H_2O molecule [36].

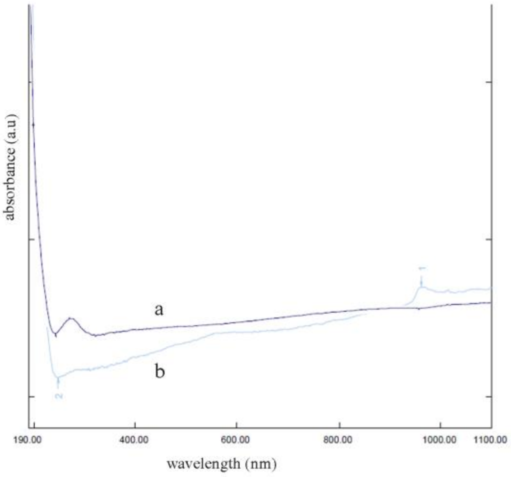

Figure 4. The electronic absorption spectra of the synthesized $Cd_{1-x}Ce_xO$ micro size layer, (a) x = 0.05 and (b) x = 1 mole%.

Peak at 1646 cm^{-1} is corresponding to carbonate [35]. Also we know that the peaks in the range from 800 to 1400 cm^{-1} are assigned to CdO [37]. The Peak at 1541 cm^{-1} is corresponding to residual organic components [38]. The peaks at 880, 1420 and 1541 cm^{-1} are corresponding to CeO_2 [2].

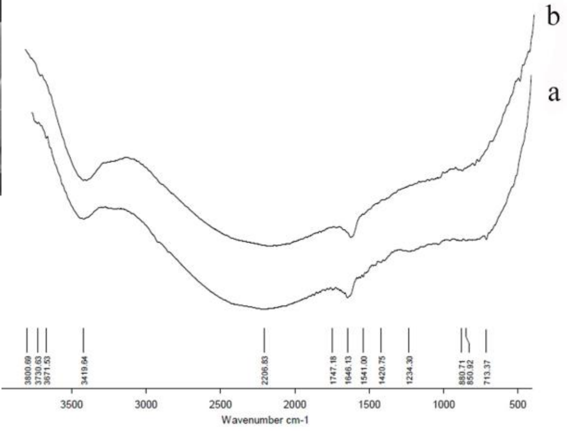

Figure 5 FT-IR spectrum of the synthesized $Cd_{1-x}Ce_xO$ sub-micron materials obtained after 12 h at 900 °C.

5. Conclusion

In summary, sub-micron materials of Ce^{4+}-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 SEM images, with doping Ce^{4+} morphology of CdO was changed from layer like to spherical cluster structure. With increasing the dopant concentration, the morphology of the cluster like structure changed to partially layered like structure. We found that compared to those of the particles of pure CdO, the diffraction lines in the powder XRD patterns of the sub-micron materials of Ce^{4+}-doped

CdO shifted to higher 2θ values. The synthesized materials exhibited electronic absorption optical properties in the UV-visible region, which showed the structure dependence on the dopant amounts Also, cell parameter refinement calculations that the unit cell contraction happened upon doping Ce^{4+} in CdO. These materials are expected to have a potential application in semiconductor devices, as catalysts, etc.

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