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# Structural, electrical, and optical absorption properties of $La_xCd_{1-x}O$ solid solution films obtained by sol–gel method

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ABSTRACT

Cadmium acetate $Cd(CH_3COO)_2{\cdot}2H_2O$ and lanthanum nitrate $La(NO_3)_3{\cdot}6H_2O$ were used to prepare the sol in the present investigation. A series of heavy La-doped CdO thin films have been prepared on amorphous glass and single-crystal Si(1 0 0) substrates by sol–gel method. The spin coater technique was employed and the prepared films were pre-annealed at 400 °C. The films were characterised by energy dispersion X-ray fluorescence (EDXRF), X-ray diffraction (XRD), UV–vis-NIR absorption spectroscopy, and dc-electrical measurements. The EDXRF spectrum was used to determine the at.% of La doped into CdO lattice. The structural study by XRD indicates that $La^{3+}$ doping grows the CdO lattice parameter due to its relatively larger standard ionic radius, 0.115 nm vs. 0.097 nm for $Cd^{2+}$. It was observed that La-doped film with 27 at.% was growing on Si substrate as an almost single crystal of [1 1 1] orientation. Then, as the doping level increased to 31 at.%, $La_2O_3$ nanograins were formed together with La-doped CdO grains. This was explained according to Hume–Rothery (HR) rules and the concept of electronegativity. The electrical measurements indicates that resistivity of crystalline samples grows very strongly with increasing at.% of La doped into CdO structure. The optical absorption studies show that $La^{3+}$ in large concentration increases the absorption coefficient in the visible region and widens the bandgap from 2.42 to more than 3 eV.


## 1. Introduction

CdO is a n-type semiconducting material with a bandgap energy between 2.2 and 2.7 eV [1,2] and a high electrical conductivity ($10^2$ to $10^3$ S cm$^{-1}$) [3]. It is a translucent in the visible region. It has a cubic structure (NaCl, monteponite structure) of a standard lattice constant 0.4692 nm [4]. Therefore, it is strongly considered in the production of solar cells, smart windows, optical communications, flat panel display, and other optoelectronic applications [5–10]. Moreover, CdO can also be used as a heat mirror due to its high reflectance in the infrared region, together with high transparency in the visible region [11]. Many methods have been employed to prepare CdO thin films like sputtering [12,13], thermal evaporation [14,15], laser ablation [16], spray pyrolysis [17,18], sol–gel [19], MOCVD [20], etc. By using metallorganic molecular-beam epitaxy method [21] and vapour-phase reaction [22], it was grown a CdO single crystals. However, CdO is usually employed after its doping with different elements like In [20], Sn [9,10], F [23,24], Al [25], Sc [26], and Y [27] in order to increase its bandgap with enhancing its electrical conduction. To our best knowledge, doping of CdO with rare-earth elements is absent from literature. However, recently [23] optical and structural properties of La-doped ZnO prepared by sol–gel method was studied. The aim of the present investigation is to study the effect of a heavy doping by lanthanum on the structural, optical absorption, and electrical properties of CdO.

## 2. Experimental

Sol–gel spin coater technique was employed to prepare thin films on clean Corning 2947 glass and Si wafer substrates. For sol preparation, the precursor solution was prepared from cadmium acetate $Cd(CH_3COO)_2{\cdot}2H_2O$ and lanthanum nitrate $La(NO_3)_3{\cdot}6H_2O$ in the following procedure. 0.3 M cadmium acetate (7.9956 g) (GPR-BDH minimum assay 98%) and an equivalent of 1%La in lanthanum nitrate (BDH-Spectrosol, maximum assay 98%) were added to 100 mL of isopropyl alcohol (2-propanol) (BDH-Analar, minimum assay 99.7%). The mixture in a 250 mL round bottom flask was fitted on a heating mental and was heated under reflux in the presence of anti-bumping granules (Fluka, Chemika) at 80 °C for 1 h. After refluxing for 1 h, the solution was transferred into a clean beaker and was stirred for half an hour. It was left to cool to room temperature for aging. The pH of the solution was 3.45. The above procedure was repeated separately with an equivalent of 2%La, 4%La and 6%La. The pH of the above reaction mixtures were within the range of 2.66–2.69. All the glassware used in this work was rinsed with deionised water and then with pure isopropyl alcohol.

Films were coated onto Corning glass and Si substrates using a spin coater operated at 2500 rpm for 1 min. The coated films were dried at 120 °C for 15 min for gel formation. Then the gel film was heated at 400 °C for 60 min. The films investi-

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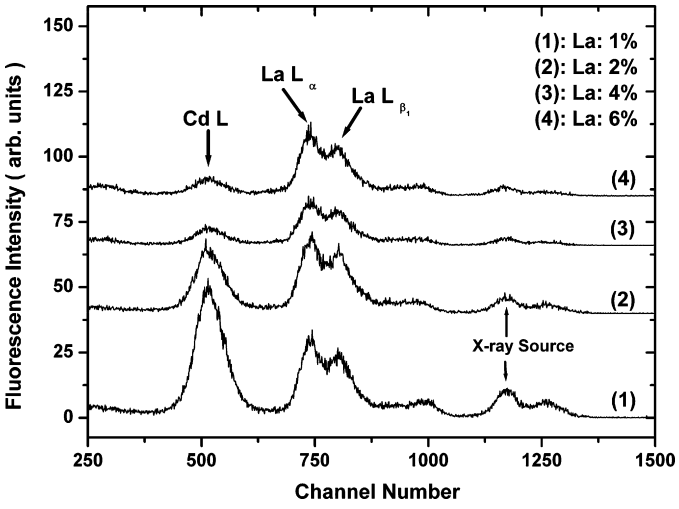


**Fig. 1.** Energy dispersion XRF spectrum of La-doped CdO thin films grown on Si substrate. The exciting radiation was Ni-filtered Cu Kα-line.

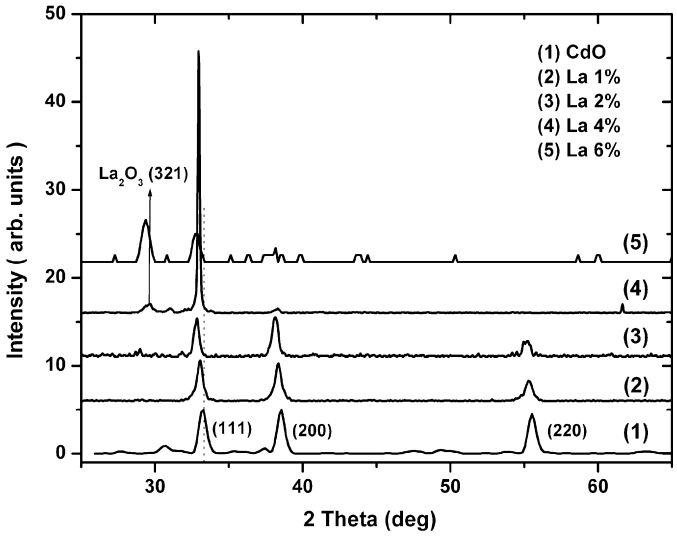


**Fig. 2.** X-ray diffraction pattern from La-doped CdO films prepared at different doping levels.

**Table 1**
The nominal % of La in constituent solution (% La-solution) and the final La molar% (at.%La) in the prepared La-doped CdO films measured by EDXRF method

| Sample | La-solution (%) | $I_r$ | at.%La |
|---|---|---|---|
| (1) | 1 | 0.81 | 13.6 |
| (2) | 2 | 1.64 | 24.2 |
| (3) | 4 | 3.53 | 27.0 |
| (4) | 6 | 5.25 | 31.0 |

gated were normally obtained by one course of spin coating, however, when thicker films for resistivity measurements were required, ten spin coating cycles for all samples were done. The thicknesses of the films were measured by a Gaertner L117 ellipsometer to be in the range 0.3–0.4 μm.

The used Si(1 0 0) substrates were cleaned by a standard technique with potassium hydroxide solution, acetone, and deionised water. The structural and compositional properties were characterised by X-ray diffraction (XRD) and energy dispersion X-ray fluorescence (EDXRF) spectrometry. The XRD measurements were carried out on Philips PW 1710 $\theta$–$2\theta$ system with Cu Kα radiation (0.15418 nm) at 35 keV and 40 mA. The EDXRF setup used a Ni-filtered X-ray beam from Cu anode and Amptek XR-100CR detector. The spectral transmittance $T(\lambda)$ and reflectance $R(\lambda)$ were measured with a Shimadzu UV-3600 double beam spectrophotometer. The dc measurements were done with Keithley 614 electrometer.

## 3. Results and discussion

### 3.1. Film composition and structure

Fig. 1 shows the EDXRF spectrum of the prepared thin La-doped CdO film on Si substrate. The spectrum demonstrates the Cd L-spectrum (3.133–3.528 keV) and La L-spectrum (4.650–5.38 keV) with some signals from the source equipment. The ratio of integral intensities of La L-signal ($I_{La}$) to Cd L-signal ($I_{Cd}$) or $I_r = I_{La}/I_{Cd}$ was used to determine the relative weight fraction ratio ($r$) of La to Cd in the film. For that purpose, the known method of micro-radiographic analysis [28,29] was used. The reference samples were pure La thin film and pure CdO film. The results are given in Table 1, where the nominal %La was taken in the solution during the preparation and at.%La is the final La molar concentration as measured by EDXRF, which describes the La doping level in the CdO sample.

The results of XRD study are shown in Fig. 2, revealed that La-doped CdO samples: 1%, 2%, 4%, and 6% were crystalline when annealed at 400 °C, however, they were amorphous when annealed at temperatures equal of less than 350 °C. Samples 1% and 2% were polycrystalline. Sample 4% has become almost a single crystal of [1 1 1] orientation when was grown on Si substrate but it was a polycrystalline on glass substrate. The energy favorable [1 1 1] preferred-orientation growth was usually observed for the growth of pure CdO prepared by different methods [12,31,33,34]. Although the Sample 4% has mainly one phase, its XRD shows the beginning of formation of $La_2O_3$ of cubic Ia3 structure of lattice constant 1.13 nm, which is close to the known value 1.1348 nm [32]. The formed $La_2O_3$ grains were grown in size by increasing the La content towards Sample 6%. The average X-ray grain size (gs) was estimated from the strongest CdO(1 1 1) reflection by using Scherrer's relation [35] and the results are given in Table 2. The grain size of formed $La_2O_3$ was 14.7 nm in the Sample 4%, which increased slightly to 20.6 nm in 6% sample. This means that Sample 6% can be considered as a nanocrystalline mixture sample since it consists of a mixture of nano-$La_2O_3$ grains with nano-La-doped CdO grains. In general, the patterns show cubic structure of CdO of lattice constant 0.467 nm as calculated from reference CdO film, which is almost identical with that of Refs. [4,12,30,31]. The strongest peak (1 1 1) in the pattern of the La-doped CdO films are shifted toward lower Bragg angles relative to that of pure CdO (33.15°) reflecting a slight increasing of lattice constant due to structural micro-stresses produced mainly by doped lanthanum atoms. Hence, the present experiments indicate that $La^{3+}$ cause CdO lattice parameter to grow due to its relatively larger standard ionic radius, 0.115 nm vs. 0.097 nm for $Cd^{2+}$ (filled shell configuration). La doping has another effect, which

**Table 2**
The crystalline-structure state, the average X-ray grain size gs ($gs_{1\,1\,1}$) calculated from CdO(1 1 1) reflection, the Bragg angle of strongest CdO(1 1 1) reflection, the optical energygap, and the Urbach's energy for the prepared La-doped CdO film samples

| Sample | La-solution (%) | Crystalline state | $gs_{1\,1\,1}$(nm) | $2\theta^{\circ}_{1\,1\,1}$ | $E_g$ (eV) | $E_U$ (eV) |
|---|---|---|---|---|---|---|
| (1) | 1 | Polycrystalline | 34.5 | 33.09 | 3.42 | 0.92 |
| (2) | 2 | Polycrystalline | 51.7 | 32.88 | 3.85 | 0.67 |
| (3) | 4 | ~Single crystal | 165.4 | 32.95 | 3.25 | 0.31 |
| (4) | 6 | Nanocrystalline | 11.4 | 33.07 | 3.0 | 0.25 |