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Optical and structural characterization of CdSe:Eu films at different volumes of europium concentration

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Abstract
Cadmium selenide films were prepared at different volumes of dopant (Europium) concentration by electrostatic-spray-pyrolysis technique. Optical results reveal low absorption and reflection with a corresponding high transmission in the visible region. Strong blue-shift is observed for the band gap energy in all cases of growth, indicating quantum confinement effect. Scanning electron studies reveal relatively smooth surface with small-sized grains on the surface. XRD confirms the crystalline nature of the films having hexagonal (wurtzite) structure with reduction in crystallinity of the film at increased volume of dopant concentration. EDX analysis confirmed the growth of CdSe:Eu film.

Keywords
Hexagonal, Wurtzite, Electrostatic, Spray pyrolysis, Nanomaterials, Optical.

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1. Introduction

Semiconductor-based devices have proved useful in vast areas including solar cells fabrication, optical fiber communications, electronic device fabrication, etc. The study of semiconductors at the nanoscale has proved over the years that nanomaterials display unique characteristics different from the bulk phase. It is based on this premise that more research is done on nanomaterials to fully understand their functions. Semiconductor particles exhibit characteristics (change in optical properties and enhanced energy gap) that are dependent on size; hence they stand amongst the important technological materials [1].
Cadmium selenide (CdSe) fit into the II-VI class of semiconductors having eight (8) valence electrons. It has immense relevance in solar cells, optoelectronics and lasers. Europium (Eu) has nine (9) valence electrons and characterized by unique optical and photoluminescence properties. Regarding the properties exhibited by europium, it is expected that doping CdSe with Eu will produce a new material with improved functions. CdSe has been previously synthesized by chemical process [1–4], electro-deposition [5] and thermal evaporation [6].
Europium-doped cadmium selenide (CdSe:Eu) find applications in optoelectronics [7] and as a sensitizer in chemiluminescence (CL) system [8]. CdSe:Eu has been synthesized by microwave synthesis [7] electrostatic spray pyrolysis [9] and sono-chemical route [10].
In the literature, very few reports [7–11] on CdSe:Eu synthesis are available. The optical properties of CdSe:Eu films at different temperatures synthesized by electrostatic spray pyrolysis [9], the growth of CdSe;Eu nanoparticles using sono-chemical route [10] and the growth of CdSe:Eu nanocrystals by substituting Cd(III) ions with Eu ions in the lattice [11] have been reported. Applications of CdSe:Eu include opto-electronics, sensitizer in CL systems and solar cells.
This research focused on CdSe:Eu synthesis by electrostatic-spray-pyrolysis at different volumes of Eu concentration, which is unavailable in previous literatures.

2. Experimental

The growth of CdSe:Eu by electrostatic-spray-pyrolysis has been reported [9]. The spray solution contains cadmium acetate dehydrate (0.4M), hydrochloric acid (stabilizer), selenium (IV) oxide (0.4M) and Europium tri-oxide (0.1M) at separate volume concentrations (10%, 15%, 20%, 25% and 30%). The solution was mixed rigorously by a magnetic-stirrer hotplate to allow for uniformity. The uniform solution (in each case) was sprayed through a spray nozzle (connected to a syringe pump) on a heated glass substrate at a stable temperature of 360^{o}C. The deposition time and flow rate were kept stable at 10 mins and 400 micro-litre/spray. Applied voltage was kept stable at 7 kV which proved to be more convenient for the deposition of the films. The optimized nozzle-substrate distance was 7.98 mm. Absorbance measurements were obtained via UV-VIS spectrophotometer in the wavelength range of 200 nm to 800 nm. Transmittance and reflectance were calculated from absorbance values. X-ray diffraction was performed by an X'pert pro x-ray diffractometer with scanning angles between 0^{o} and 80^{o}. Scanning electron microscopy (SEM) was executed using a Carl-Zeiss scanning electron microscope, while energy dispersive analysis x-ray spectroscopy was done using the facility fixed to the SEM equipment.

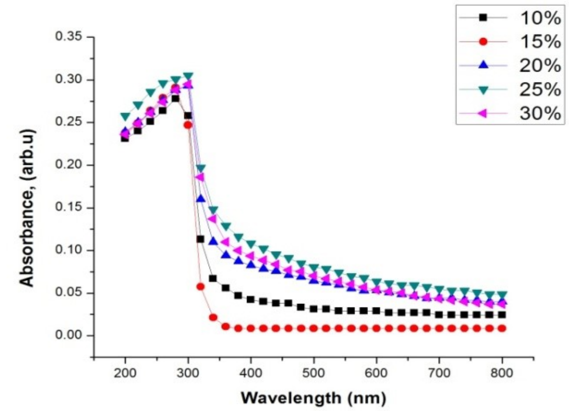

Figure 1. Absorbance spectra of CdSe:Eu .

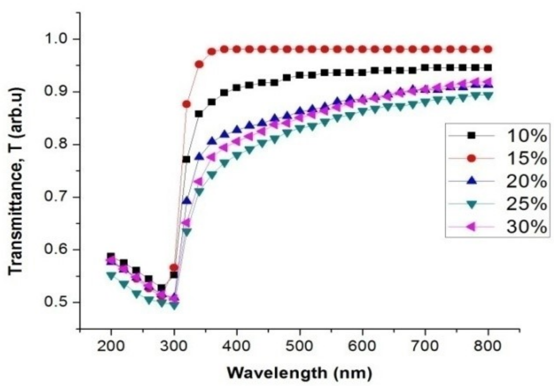

Figure 2. Transmittance spectra of CdSe:Eu .

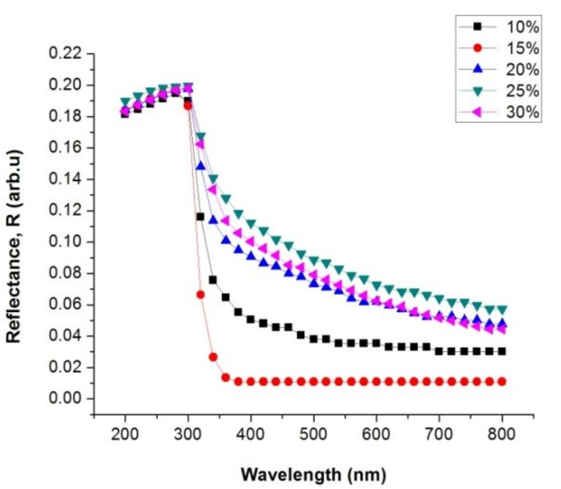

Figure 3. Reflectance spectra of CdSe:Eu .

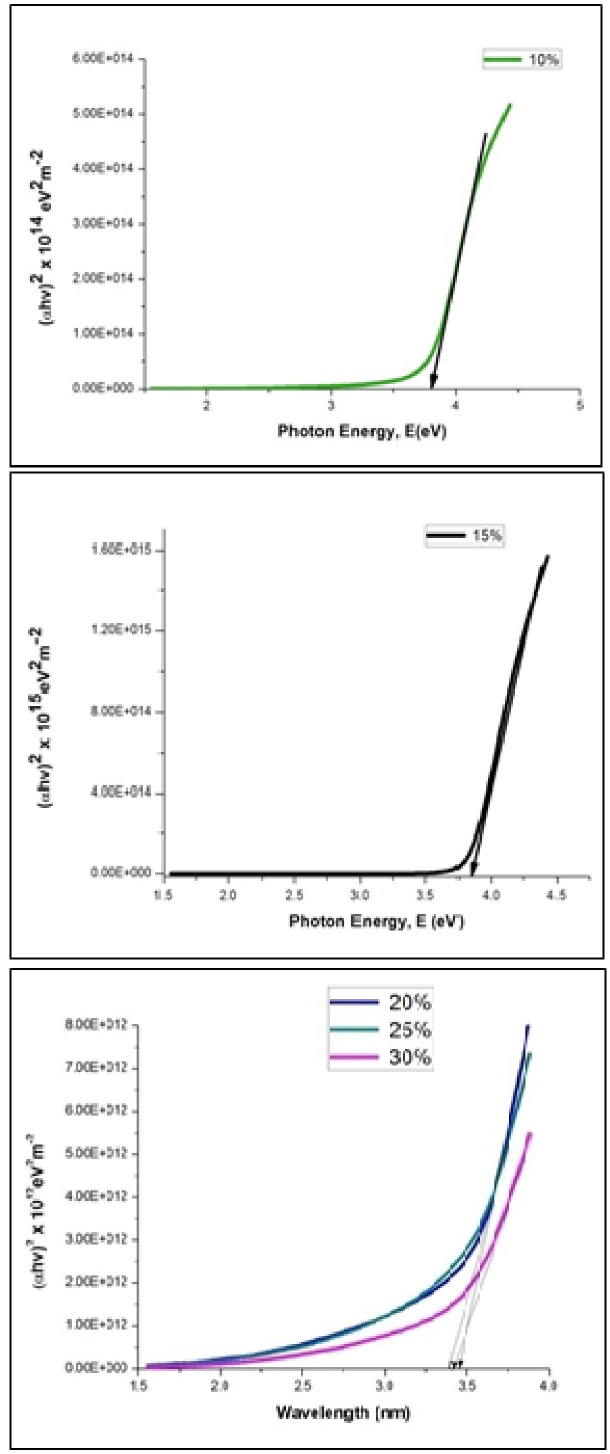

Figure 4. (a)Plot of $(\alpha h\nu)^2$ versus photon energy for CdSe:Eu at 10% volume concentration.(b)Plot of $(\alpha h\nu)^2$ versus photon energy for CdSe:Eu at 15% volume concentration.(c)Plot of $(\alpha h\nu)^2$ versus photon energy for CdSe:Eu at 20%,25% and 30% volume concentrations

3. Results and discussions

The optical, structural and EDX results are presented in this section and analyzed accordingly.

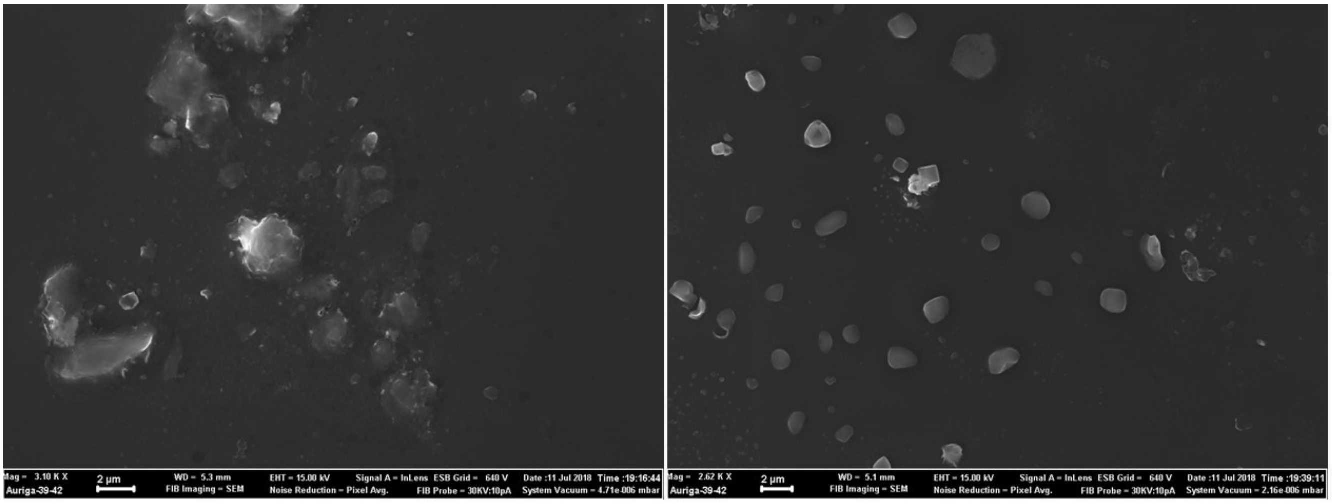

Figure 5. (a)SEM image of CdSe:Eu at 10%.(b)SEM image of CdSe:Eu at 15%.

The CdSe:Eu displayed poor absorption all through the UV and VIS regions. In the UV region, between 10% and 31% absorption is observed, while for the VIS region, between 0.1% and 10% is observed. The exhibited peaks in the absorption spectrum around 270 nm and 300 nm suggest the presence of defect states within the crystal lattice of CdSe:Eu. Such defects states are very vital in electronic transitions within the material. Due to the large dopant concentrations, states within the conduction band becomes populated, hence, pushing the absorption edge to higher energies and subsequently increases the band gap energy.

The CdSe:Eu deposited at different dopant concentrations recorded low transmittance from 49.81% to 59.84% in the UV-region while the films have high transmittance between 73.08% to 97.63% in the VIS-region as shown in figure 2.

The transmittance of CdSe:Eu films in the VIS-region at different deposition conditions indicates that CdSe:Eu will prove very useful in the manufacture of glasses, vehicle windscreens, optical lenses, windows and optoelectronic devices. The results obtained in this research share similarity with those by [10] for spray-deposited CdSe films. Also, the results displayed high transparency for CdSe:Eu in the VIS-region which agrees with the report of [12]. However, the transparency of CdSe:Eu deposited in this work appear to be higher compared to those obtained by [12, 13]. This observation may arise from the addition of rare-earth impurity (europium) to the pure CdSe in this research.

From figure 3, all the reflection spectra exhibited a descending trend in the VIS-region as wavelength increases. For the films deposited at 10% and 15% dopant concentration, reflection values all through the UV-region were from 6.33% to 19.12% and 1.76% to 19.32% respectively. For the films deposited at 10%, the reflection values were within 2.96% and 5.18% in the VIS-region while for the films deposited at 15% dopant concentrations, reflection value was constant at 1.33% in the VIS-region. For the films deposited at 20% dopant concentration, reflection values recorded in the UV-region and visible region were within 10.61% to 19.69% and 4.48% to 8.91% respectively. Films deposited at 25% and 30% dopant concentrations have reflection values from 5.84% to 19.92% and 4.4% to 19.81% throughout the UV-VIS regions. It is pertinent to observe that in all cases of variations, all the deposited films of CdSe:Eu exhibited poor reflection of light throughout the entire UV-VIS regions. This characteristic of poor reflection exhibited by CdSe:Eu makes it a choice material as anti-reflective coating in solar cells.

The band gaps for CdSe:Eu were obtained by extrapolation of the straight portions of the curves in figures 4a – 4c.

Band gap varies between 3.35 eV and 3.80 eV at varying concentrations. A descending trend in band gap from 3.8 eV to 3.35 eV as volume concentration increases from 10% to 25% volume concentration is observed. However, at 30%, a band gap value of 3.4 eV is attained. Such trend could have resulted due to perceived existence of defect states within the crystal lattice. Band gap values from this research exhibited very strong blue-shift from that of bulk CdSe. This could be ascribed to quantum confinement existence resulting from the nanosized grains reported.

From figures 5a and 5b, the films appear to have a smooth surface morphology. A very close look at the SEM images reveals very small spherical shapes (though, not uniformly spread) which indicate the growth of small crystallites on the film's surface.

Figures 6a and 6b display the XRD image of CdSe:Eu obtained at a substrate temperature of 360^{o}C, 10% and 20% dopant concentrations respectively.

From figure 6a, the observed diffraction peaks obtained at 2θ values of 28.93^{o}, 30.62^{o}, 34.98^{o} and 51.05^{o} are indexed to the diffraction planes; (100), (101), (102) and (103) which is very close to reported standard values in the JCPDS-15-0105 card number.

From the XRD pattern, the films presents crystalline characteristics and the indexed planes (miller indices or hkl values) suggests a hexagonal (wurtzite) structure for the synthesized

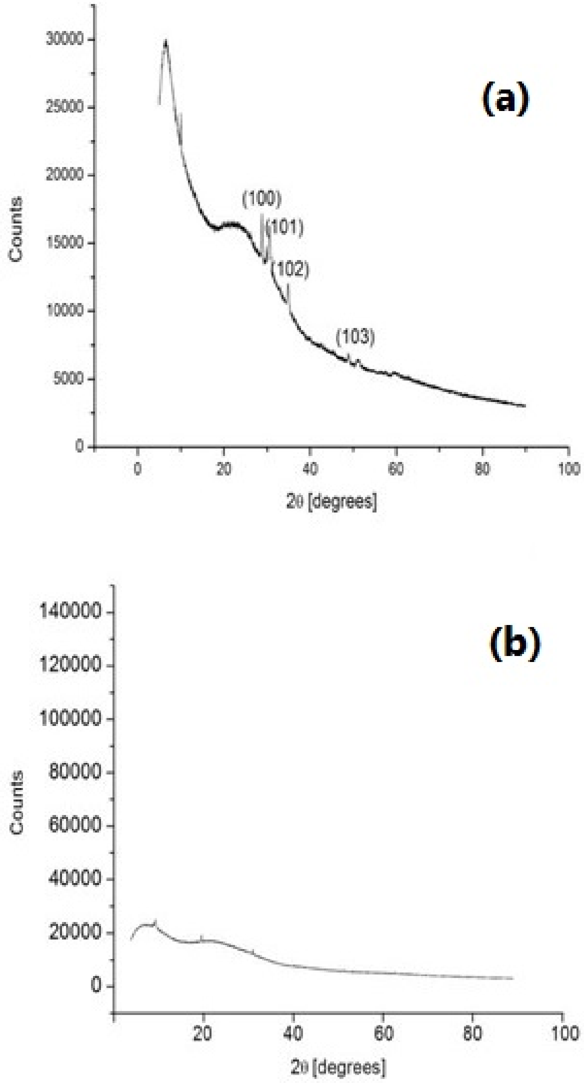

Figure 6. (a)XRD image of CdSe:Eu at 360^{o}C and 10% dopant concentration.(b)XRD image of CdSe:Eu at 360^{o}C and 20% dopant concentration.

CdSe:Eu. The crystallite size corresponding to 2θ values of 28.93^o, 30.62^o, 34.98^o and 51.05^o are 38.95 nm, 25.30 nm, 24.16 nm and 21.89 nm respectively.
From figure 6b, no peaks were observed.
Peaks corresponding to cadmium (Cd), selenium (Se) and europium (Eu) are obvious from the EDX spectra in figure 7 which indicate the growth of CdSe:Eu film. The peaks assigned to Si, Na, and K are results from the substrate (glass slides) used for the deposition process. The chlorine (Cl) peak results from the HCl used in the deposition process while the oxygen (O) peak is possibly due to atmospheric exposure.

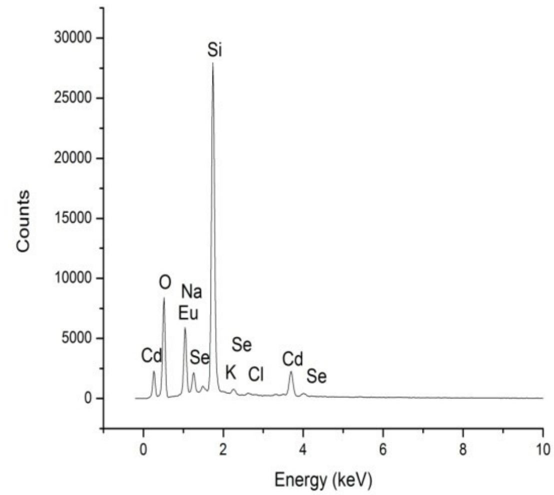

Figure 7. (a)EDX spectra of CdSe:Eu obtained at 360^{o}C and 10% dopant concentration.

4. Conclusion

Results and discussions based on synthesizing CdSe:Eu electrostatically have been presented. Absorption peaks evident in the VIS-region suggests evidence of defect states within the crystal. Increase in band gap results from quantum confinement effects. Micro-structural analysis shows formation of small nanosized grains, while XRD reveal the crystalline nature of CdSe:Eu. The properties exhibited by the grown films suggest their suitability in the fabrication of anti-reflective coating for solar-cell applications, optical windows and lenses.

Conflict of interest statement:
The authors declare that they have no conflict of interest.

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