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Optical Properties of ZnO – CdS Nano Composites

K.U. Madhu, T.H. Freeda, and C.K.Mahadevan
[1.]Physics Research Centre, S.T. Hindu College, [2.]Nagercoil 629 002, Tamil Nadu, India.

Abstract: - Over the past few years, more effort has been taken to synthesise various inorganic nanocrystalline materials with different sizes and shapes due to their interesting properties and applications. In the present work we have prepared $(ZnO)_x$ $(CdS)_{1-x}$ nano composites by the solvothermal method using a domestic microwave oven. All the prepared (7 with x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0) samples were optically characterized by UV-Vis – NIR spectral, photoconductivity and photoluminescence measurements.

From the UV-Vis-NIR spectra the band gap energies were calculated. It is found that they were slightly higher than the reported values for the end members in the bulk state. This significant change can be attributed to the quantum confinement of the ZnO and CdS nanoparticles. For mixed nano composites the band gap energy lies between the end members. The absorption band region was also determined from the spectrum. The photo conductivity measurements were made for all the samples and a positive photoconductivity was observed for all the samples. The results indicate that the ZnO-CdS nanocomposites are very photosensitive. Photoluminescence studies carried out exhibit five prominent peaks with different wavelengths. The results are reported.

I. INTRODUCTION

II – VI compounds as a collective group of materials have been and still are the subject of much intensive investigation. The growth of semiconductor technology in the early 1950's highlightened the limitations of silicon and germanium of which perhaps the character and the magnitude of the forbidden energy gap were the most disadvantageous. At first the extension in the range of energy gaps was sought in the III –V compounds, where considerable success has been achieved with InSb and GaAs in the low and high energy gap areas respectively. GaAs is today probably the most developed and well understood compound in existence. Concurrently with the later developments in the III-V compounds, systematic studies were made for several of the II-VI compounds. The results of these studies have revealed much about the general nature of the II-VI compounds and the feature of chemical stability of the higher energy gap materials at room temperature offers an immediate advantage over the unstable III - V phosphides. II – VI compounds in their broadest sense includes compounds formed from elements of group II and group VI of the periodic table.

ZnO is a II – VI compound semiconductor. The properties such as wide bandgap, large exciton binding energy and low threshold power for optical pumping are considered to be the eminent features of ZnO. So zinc oxide is said to be efficient phosphor [1 – 4].

Cadmium sulphide is also important semi conductive II – VI compound material having a typical wide band gap of 2.42 eV at room temperature and exhibiting excellent optical properties and various luminescence properties such as photoluminescence (PL) and electroluminescence (EL). Its wide applications involve laser light emitting diodes, solar cells and other optical devices based on its nonlinear properties [5-13]. Moreover it finds potential application in the field of Bio imaging [14 - 18]. It is well known that those fantastic properties of nanoscale semi conductive materials are dependent on size, shape and crystallinity. There are various methods to synthesise ZnO and CdS nano crystals such as solvothermal, hydrothermal, self assembly, sol–gel, etc.[19 – 23] and currently researches are going on in finding out new methods. The preparation of ZnO- CdS nanocomposites have been already reported[24]. In the present work we have optically characterized the prepared ZnO- CdS composite nano powders. We report herein the results obtained

II. PREPARATION OF SAMPLES

Analytical reagent (AR) grade zinc acetate, cadmium acetate, thiourea and urea along with doubly distilled water were used for the preparation of $(ZnO)_x$ $(CdS)_{1-x}$ nanocrystals. For preparing ZnO (for x=1) zinc acetate and urea taken in the 1:3 molecular ratio were dissolved in 100 ml doubly distilled water and kept in a domestic microwave oven (operated with a frequency 2.45GHz and power 800W). Similarly, for the preparation of CdS nanocrystals (x=0.0), the cadmium acetate and thiourea were used in the place of zinc acetate and urea. Required amounts of precursors were used for the preparation of mixed systems.

Microwave irradiation was carried out till the solvent was evaporated until the colloidal precipitate was obtained. The colloidal precipitate thus obtained was cooled, washed with doubly distilled water for six times and then with acetone to remove the organic impurities present, if any. The sample was then dried at room temperature and collected as yield.

A total of 7 samples were prepared with x having the values 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0. In order to improve the ordering the samples were annealed at 100 °C for about 1 hour for all the samples.

III. UV-VIS-NIR SPECTRA

The UV-Vis-NIR optical absorption spectra for all the seven samples were recorded and they are shown in Figures 1(a to g) From the spectra the band gap energy was calculated using the relations.

$$E_g = h\upsilon \quad \text{and} \quad \upsilon = c/\lambda.$$

where h is the Planck's constant, c is the velocity of light in air (3×10^8 m/s) and λ is the absorption wavelength in nm. The optical band gap energies and the absorption band region obtained in the present study are provided in Table 1.

Table 1: Band gap energies and absorption band regions

System(with expected composition)	Band gap energy (eV)	Absorption band region (nm)
ZnO	4.69	223 – 298
$(ZnO)_{0.8}$ $(CdS)_{0.2}$	2.91	240 – 428
$(ZnO)_{0.6}$ $(CdS)_{0.4}$	2.85	284 – 437
$(ZnO)_{0.5}$ $(CdS)_{0.5}$	2.73	321 – 527
$(ZnO)_{0.4}$ $(CdS)_{0.6}$	2.57	244 – 500
$(ZnO)_{0.2}$ $(CdS)_{0.8}$	2.53	333 – 490
CdS	2.53	301 – 492

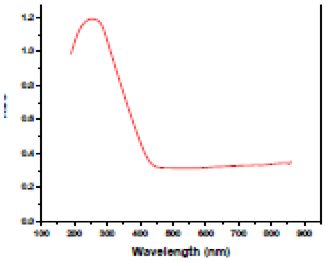


Fig : 1a

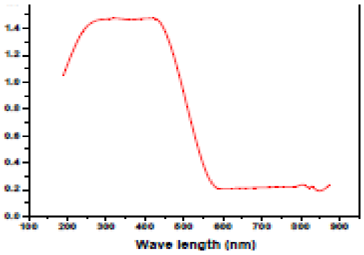


Fig : 1b

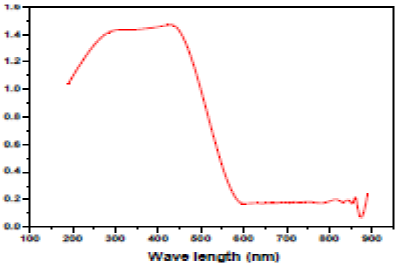


Fig : 1c

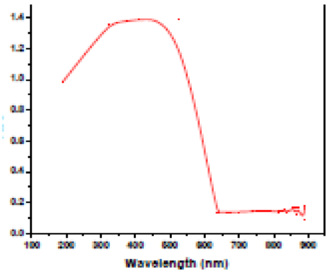


Fig : 1d

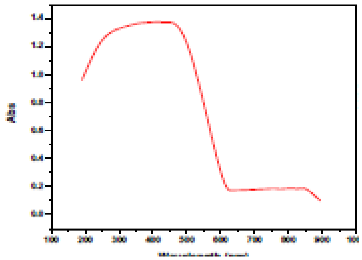


Fig : 1e

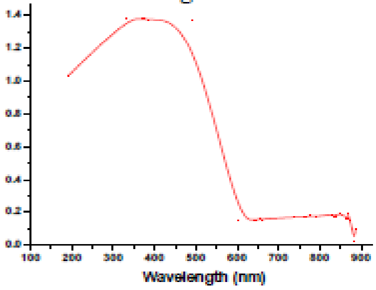


Fig : 1f

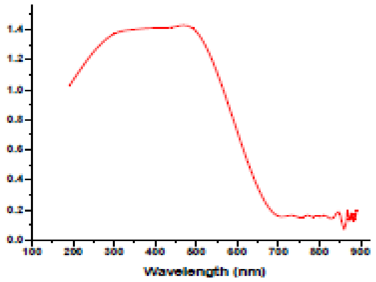


Fig : 1g

Fig 1a : UV-Vis-NIR spectrum for pure ZnO
Fig 1b : UV-Vis-NIR spectrum for $(ZnO)_{0.8}$ $(CdS)_{0.2}$
Fig 1c : UV-Vis-NIR spectrum for $(ZnO)_{0.6}$ $(CdS)_{0.4}$
Fig 1d : UV-Vis-NIR spectrum for $(ZnO)_{0.5}$ $(CdS)_{0.5}$
Fig 1e : UV-Vis-NIR spectrum for $(ZnO)_{0.4}$ $(CdS)_{0.6}$
Fig 1f : UV-Vis-NIR spectrum for $(ZnO)_{0.2}$ $(CdS)_{0.8}$
Fig 1g : UV-Vis-NIR spectrum for pure CdS

The optical band gap energy reported in the literature [25] for ZnO is 3.37 eV and that for CdS is 2.42eV. But in the present study, significantly higher values have been observed (4.69eV for ZnO and 2.53 eV for CdS). This significant change can be attributed to the quantum confinement of the ZnO and CdS nanoparticles. For the mixed nanocrystals(nanocomposites), it is observed that the band gap energy lies between the end members.

Borse et al [26] have observed for CdS thin films the band gap energy of 2.34 eV. The band gap energy observed in the present study for the quantum dots are significantly more than that observed by Borse et al [26] for their films. Also, the band gap energies observed in the present study for ZnO and CdS quantum dots are significantly more than that for the bulk crystals of ZnO and CdS as mentioned above. The increase in band gap energy may be attributed to the reduced particle (grain) size.

In semiconductors, the Fermi level lies between two bands, so that the edges of bands are dominating the low energy optical and electronic behaviour. Optical excitations across the gap depends strongly on the size even for crystallites as large as with 10,000 atoms. The quantum size effect is most pronounced for the semiconductor nanoparticles, where the band gap increases with decreasing size, resulting in the inter band transition shifting to higher frequencies. In a semiconductor, the energy separation, i.e. the energy difference between the completely filled valence band and the empty conduction band is of the order of few electron volts and increases rapidly with a decreasing size [27].

IV. PHOTOCONDUCTIVITIES

Photoconductivity is the tendency of a substance to conduct electricity to an extent that depends on the intensity of light-radiant energy striking the surface of a sample. The absorption of radiation of suitable frequency by any compound leads to the creation of free electron-hole pairs.Figures 2a to 2g show the variation of both the dark (I_d) and photo (I_p) currents with applied field. It is observed that both dark and photo currents of the nano composites $(ZnO)_x(CdS)_{1-x}$ (x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0), increase (very nearly) linearly with the applied voltage.

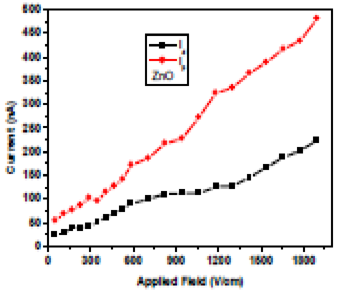


Fig: 2a

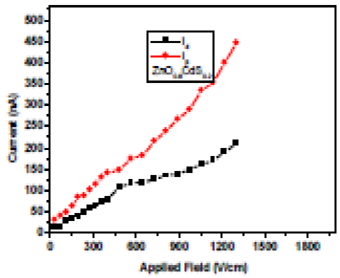


Fig: 2b

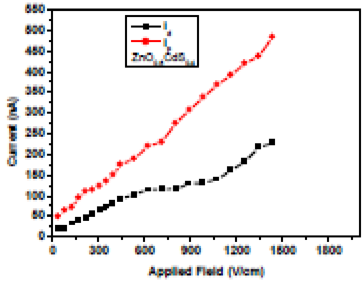


Fig: 2c

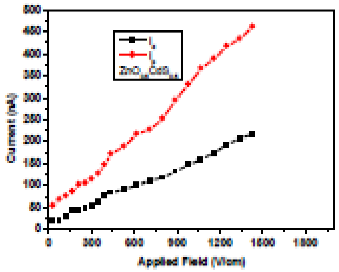
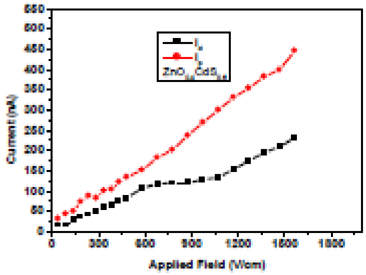


Fig: 2d



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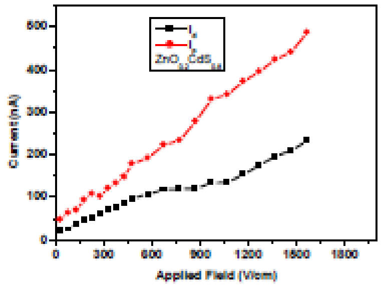

Fig: 2f

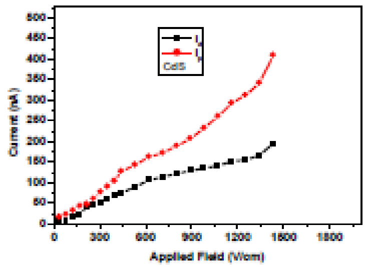

Fig : 2g

Fig 2a : UV-Vis-NIR spectrum for pure ZnO
Fig 2b : UV-Vis-NIR spectrum for $(ZnO)_{0.8}$ $(CdS)_{0.2}$
Fig 2c : UV-Vis-NIR spectrum for $(ZnO)_{0.6}$ $(CdS)_{0.4}$
Fig 2d : UV-Vis-NIR spectrum for $(ZnO)_{0.5}$ $(CdS)_{0.5}$
Fig 2e : UV-Vis-NIR spectrum for $(ZnO)_{0.4}$ $(CdS)_{0.6}$
Fig 2f : UV-Vis-NIR spectrum for $(ZnO)_{0.2}$ $(CdS)_{0.8}$
Fig 2g : UV-Vis-NIR spectrum for pure CdS

V. PHOTOLUMINESCENCE

Luminescence is the general term used for the absorption and emission of radiant energy. Photoluminescent systems are those which can be excited by electromagnetic radiations and as a consequence reemit radiations either of the same or of longer wavelengths.

The PL emission spectra recorded, in the present study, for all the seven samples are shown in Figure 3a. All the samples prepared in the present study exhibit five prominent peaks in the PL spectra. The peaks are observed at around 408,446,486,489 and 529 nm. Out of these, the peaks at 408,446 and 529 nm are dominant peaks with high intensity. The peaks at 486 and 489 nm are of less intensity as well as close by.

The comparison of the two end members (ZnO and CdS) with that of the middle composition $(ZnO)_{0.5}$ $(CdS)_{0.5}$, is shown in Figure 3b. It clearly indicates that the intensity is high for the middle composition.

The peak observed at 408 nm is known as the violet emission peak and is attributed to sulphide vacancies. This agrees well with the peak value at 428 nm reported by Becker and Bard [30]. The emission peak at 446 nm is attributed to the Zn/Cd vacancies which agree well with the work of Murase et al [31]. The emission peaks observed at 486 and 489 are known as green emission peaks of CdS. These peaks may occur due to a) combination of free electrons from conduction band with holes captured on an acceptor level, b) recombination of trapped electrons from a donor level with free holes and c) recombination of electrons from a donor level with holes trapped on an acceptor level [32, 33].

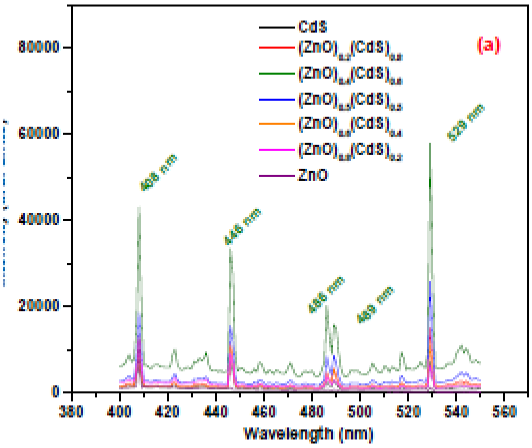

Fig 3a: PL spectra for samples prepared

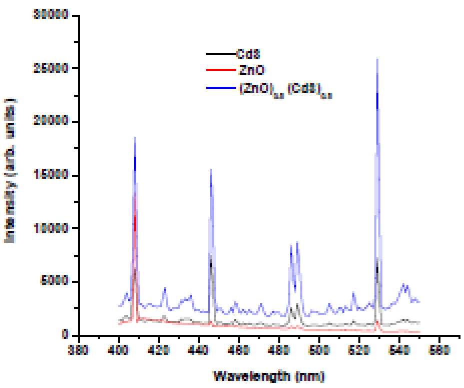

Fig 3b: Comparison with end members

The green band emission in the present study may be due to the acceptor levels related to the interstitial sulphur and donor levels due to native defects in ZnO and CdS lattices. The emission peak at 529 nm is known as yellow–green peak. This emission is the result of radiative recombination of the electrons and holes via the surface/defect states present in the nanocrystals. The electrons and holes after excitation across the band edge trickle down non-radiatively to the surface states lying in the band gap region. Radiative deexcitation across the surface states in ZnO/CdS nanocrystals gives rise to bright yellow-green emission observed at around 529 nm. Similar results have been reported already by earlier workers [34-36] for their systems.

VI. CONCLUSION

All the prepared samples were optically characterized by carrying out the UV-Vis-NIR, photoconductivity and photoluminescence measurements. The optical band gap energy is found to be significantly higher when compared to that reported in literature for the end members. This change can be attributed to the quantum confinement of the ZnO and CdS nanoparticles. From the photoconductive studies it is observed that the $(ZnO)_x$ $(CdS)_{1-x}$ nanocomposites exhibit a positive photoconductive nature. This may be due to the generation of mobile charge carriers caused by the absorption of photons. The PL emission spectra recorded for all the seven samples in the present study exhibit\ five prominent peaks.

In effect, the present study indicates that forming two component nanocomposites with ZnO and CdS leads to strong enhancement in optical properties and can be used in various photonic applications.

VII. ACKNOWLEDGEMENT

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