RESEARCH ARTICLE

SYNTHESIS AND RAMAN STUDIES OF Ce DOPED CdS NANOPARTICLES

M. Sreenivas[1], G.S. Harish[2], P. Sreedhara Reddy[3]
[1, 2, 3]Department of Physics, Sri Venkateswara University, Tirupati, 517502, India.

Manuscript Info	*Abstract*
	Ce doped CdS nanoparticles were successfully synthesized by the cost effective chemical co-precipitation method at room temperature. The structural, morphological, compositional and Raman studies were carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDAX) and high resolution Raman spectroscopic techniques respectively. Broadened XRD peaks show the formation of Ce doped CdS nanoparticles with wurtzite structure. SEM and EDAX analysis show surface morphology and elemental composition of prepared nanoparticles. The Raman spectra of undoped and Ce doped CdS nanoparticles showed longitudinal optical mode. Compared with the 1LO and 2LO Raman modes (296 and 590 cm^{-1}) of undoped CdS nanoparticles, the Raman modes of Ce doped CdS nanoparticles were slightly shifted towards lower frequency. **

INTRODUCTION

Among the II–VI group semiconductors, CdS is an important compound with a wide band gap. Compared to bulk material, reduction in the particle size to nano – range strongly influences the crystallinity, melting point, optical and structural stability. By changing the particle size of the prepared nano-sized semiconductors, they can have considerable limitations, and also have potential applications in solar energy conversion, photoconducting cells, non-linear optics, heterogeneous photocatalysis and electro-luminescence device applications due to quantum confinement [1–5]. The size - controlled nanoparticles finds interesting application in displays because they can easily be made into film devices compared to traditional phosphors.

Besides the transition metal ions, rare earth ions doped systems mainly reflect the properties of the dopant and find interesting luminescence based applications. Doping of rare earth element like cerium reduces the particle size of the nanomaterials and also increases surface area [6-8]. By using organic or inorganic capping agents, the particle size of the nanomaterial can be controlled. PVP as a capping agent plays a significant role not only to increase the stability but also for the effective doping of Mn into the CdS nanophosphors, which can be attributed to the formation of coordinate bonding groups between lone pair of oxygen atoms and those of metallic atoms Cd and Mn in the CdS nanocomposite [9, 10].

In this study, a simple and cost effective chemical co-precipitation method was described to prepare cerium doped CdS nanoparticles at different concentrations of cerium and PVP is used as capping agent. The dopant effect on structure, surface morphology, composition and Raman studies were investigated in detail. All the techniques support the effective doping of Ce into CdS host material.

EXPERIMENTAL AND CHARACTERIZATION DETAILS

All chemicals were of analytical reagent grade and were used without further purification. Undoped CdS, cerium (Ce) (1, 2 and 3 at.%) doped CdS nanoparticles were prepared by a simple chemical co-precipitation method with biocompatible polyvinylpyrrolidone (PVP) as a capping agent. The reactants were $CdCl_2$, $CeCl_3.7H_2O$ (1, 2 and 3 at.%), Na_2S and polyvinylpyrrolidone (PVP). Ultrapure de-ionized water was used as the reaction medium in all the synthesis steps. In a typical synthesis, desired molar proportions of $CdCl_2$, $CeCl_3.7H_2O$ (1, 2 and 3 at.%), each in 50 ml were dissolved in ultrapure de-ionized water**.** An appropriate amount of capping agent PVP was added to control the growth of the nanoparticles during the reaction. Later stirring the solution for 60 min, Na_2S solution was drop wisely added to the solution at room temperature under constant stirring which was continued for four hours to get fine precipitation. The obtained precipitate was washed with de-ionized water several times. Finally, the powders were vacuum dried for 3 hours at $80\ ^0C$ to obtain Ce**,** doped CdS nanoparticles. Undoped CdS nanoparticles were also synthesized by the same procedure.

The prepared nanopowders were then characterized by studying the structure, composition, surface morphology and Raman studies. The X-ray diffraction patterns of the samples were collected on a Rigaku D X-ray diffractometer using Cu-Kα radiation (λ=1.5406A°). The morphology and elemental composition of the prepared samples were analyzed through EDAX using Oxford Inca Penta FeTX3 EDS instrument attached to a Carl Zeiss EVO MA 15 scanning electron microscope. Raman Spectroscopic studies of the as prepared samples were carried out using a LabRam HR800 Raman Spectrometer.

RESULTS AND DISCUSSION

Structural analysis

The XRD patterns of Ce doped and pure CdS nanoparticles at different concentrations of Ce (1, 2 and 3 at.%) are shown in Fig. 1. The broadening of peaks indicates that particles are in the nano-size regime. The XRD pattern shows (100), (002), (101), (102), (110), (103) and (112) planes of wurtzite CdS corresponding to JCPDS File No. 41-1049. As there are no such peaks of Ce, CeS, Ce2S3, confirmed the successful incorporation of Ce3+ ions into the crystal lattice of CdS nanoparticles [8]. The intensity of the planes increases with increasing the doping concentration of Ce. In the diffraction patterns, peak broadening is due to four factors: deformation of the lattice, crystalline domain size, crystalline faults and domain size distribution [11]. From the XRD spectra it was also observed that no diffraction peaks corresponding to the impurity phases were detected and this rule out Ce precipitation or secondary phases. The average particle size calculated by Debye Scherrer's equation [9] for PVP capped Ce doped CdS nanoparticles lies in the range of 4 - 6 nm.
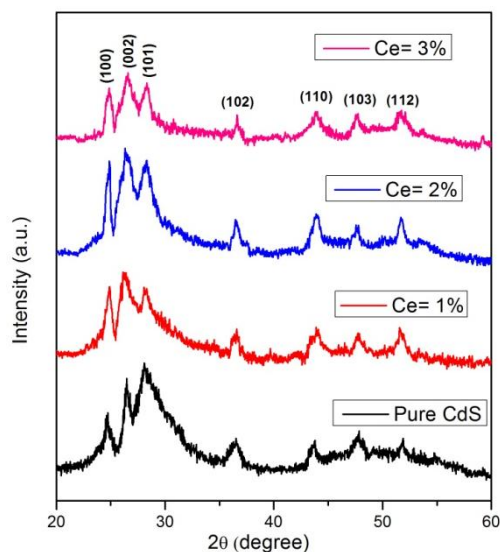

Figure 1: XRD patterns of Pure and Ce (1, 2 and 3 at.%) doped CdS nanoparticles

Morphological and Compositional analysis

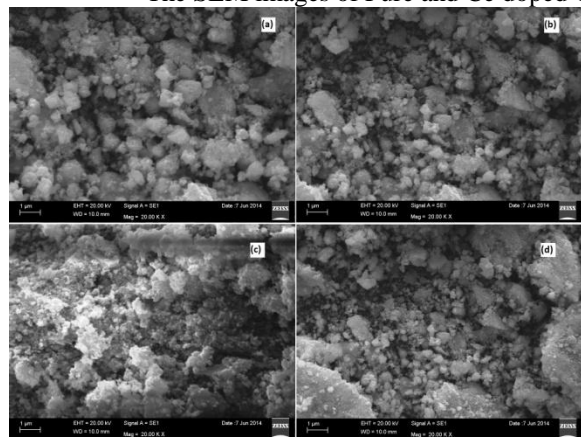The SEM images of Pure and Ce doped CdS nanoparticles are shown in Fig. 2.

Figure 2: SEM images of Pure and Ce (1, 2 and 3 at.%) doped CdS nanoparticles

Figures 2(a), 2(b), 2(c) and 2(d) show the SEM images of pure CdS, CdS: Ce (Ce =1, 2 and 3 at.%) nanoparticles respectively. SEM images showed the slightly agglomerated nanoparticles of the prepared samples and agglomeration is decreased with increasing Ce concentration.

Fig. 3 shows representative EDAX spectra of pure and Ce (1, 2 and 3 at.%) doped CdS nanoparticles. It is evident from the EDAX Spectra that no other elemental peaks other than Cd, S and Ce are observed except that only the elemental carbon arises due to adhesion of carbon tape on to the stud used in the analysis. Fig. 3 (a) shows the EDAX spectra of pure CdS. Fig. 3 (b), (c) and (d) confirm the effective doping of Ce (1, 2 and 3 at.%) into CdS host lattice.
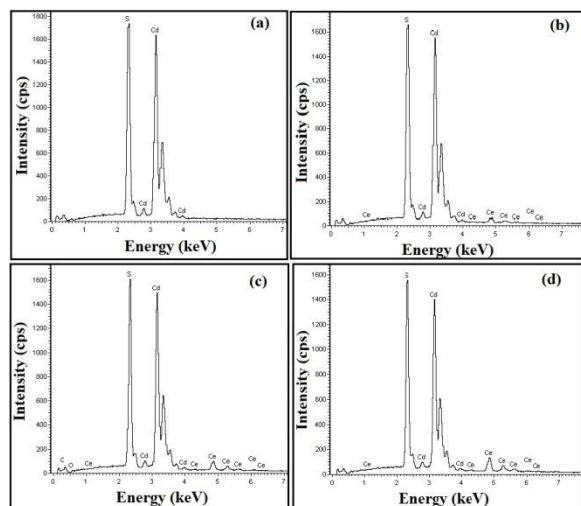

Figure 3: Representative EDAX spectra of (a) Pure CdS (b) Ce =1 at.%, (c) Ce = 2 at.% and (d) Ce = 3 at.% doped CdS: Ce nanoparticles

Raman Studies

Fig. 4 shows the Raman spectra of the undoped and Ce (1, 2 and 3at.%) doped CdS nanoparticles in the frequency range 200 - 700 cm^{-1}. In case of bulk CdS, the Raman spectrum exhibits the first longitudinal optical phonons (1LO) peak and the second longitudinal optical phonons (2LO) peak at 304 and 600 cm^{-1} respectively [12-14]. The Raman spectrum of pure CdS nanoparticles exhibited strong but broad peaks around 296 and 590 cm^{-1} corresponding to 1LO and 2LO optical phonons, respectively. In the case of large surface-to-volume ratio, surface scattering contributes more to the Raman signal than volume scattering. The frequency shifts of the 1LO and 2LO modes observed in the present samples may be attributed to a smaller size and larger surface-to-volume ratio compared with that of the undoped CdS. Another possible reason for the Raman shift is that the ionic radius of Ce^{3+} ion is higher than that of Cd^{2+} ion. Lattice defects are introduced or intrinsic host lattice defects are activated when

Ce^{3+} ions are incorporated and the Ce^{3+} ions tend to occupy substitutional cationic sites resulting in host lattice defects. Further, no additional Raman modes due impurities were observed in Ce doped CdS nanoparticles. This revealed the absence of impurity phases in the prepared nanopowder samples.
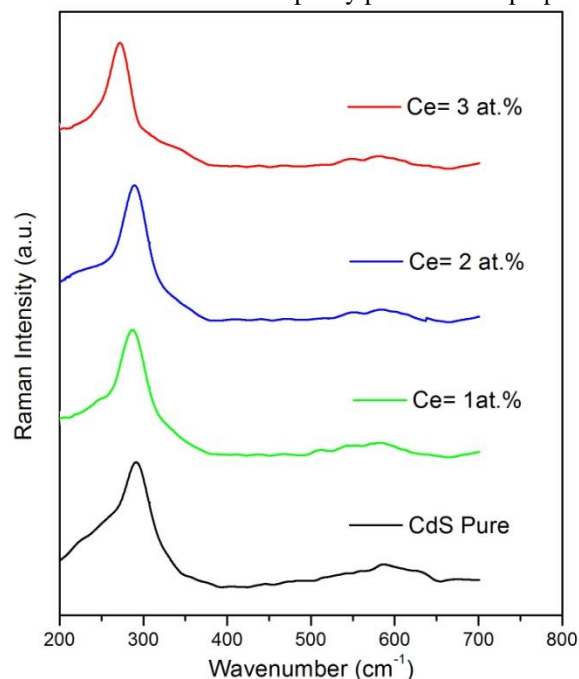

Figure 4: Raman Spectra of Pure and Ce (1, 2 and 3 at.%) doped CdS nanoparticles

CONCLUSIONS

Cerium doped CdS nanoparticles were successfully synthesized by the cost-effective chemical co-precipitation method at room temperature. The influence of dopant concentration on structural, compositional, morphological and Raman spectroscopic properties of the prepared samples was studied. XRD studies confirmed the wurtzite structure of the prepared samples. EDAX spectra showed the effective doping of cerium into CdS. Raman spectra of the pure CdS nanoparticles showed Raman peaks at 296 and 590 cm-1correspond to the 1LO mode and 2LO mode. Compared to pure CdS, Cerium doped CdS samples showed an asymmetric broadening and a slight red shift indicating phonon confinement effects.

ACKNOWLEDGEMENTS

REFERENCES:

[1] M. Rajesh Kumar and G. Murugadoss, (2014), "Synthesis and study of optical and thermal properties of Mn doped CdS nanoparticles using polyvinylpyrrolidone" Journal of Luminescence, 146, 325–332.
[2] K. Hu, M. Brust and A.J. Bard, (1998), "Characterization and surface charge measurement of self-assembled CdS nanoparticle films." Chemistry of Materials, 10 (4), 1160-1165.
[3] Y. C. Chu, C. C. Wang and C. Y. Chen, (2005), "Preparation and Characterization of Luminescent CdS Nanoparticles Immobilized on Poly (St-co-GMA-IDA) Polymer Microspheres", Nanotechnology, 16(4), 376-385.
[4] A. Cortes, H. Gómez, R.E. Marotti, G. Riveros and E.A. Dalchiele, (2004), "Grain size dependence of the bandgap in chemical bath deposited CdS thin films", Solar Energy Materials and Solar Cells, 82 (1-2), 21-34.
[5] K. Maeda and K. Domen, (2010), "Photocatalytic water splitting: recent progress and future challenges", The Journal of Physical Chemistry Letters, 1, 2655-2661.
[6] J. Liqiang, S. Xiaojun, X. Baifu, W. Baiqi, C. Weimin and F. Honggang, (2004), "Structural phase transformation of La-doped and Ce-doped TiO_2nanoparticles",Material Science and Technology, 12, 148-152.
[7] G. Guo, D. Li, Z. Wang and H. Guo, (2005), "Antibacterial characteristics of ZnO–CeO2 nanopowder prepared by laser vapor condensation", Journal of Rare Earths, 23, 362–367.

[8] L. Saravanan, A. Pandurangan and R. Jayavel, (2012), "Synthesis and luminescence enhancement of Cerium doped CdS nanoparticles," Materials Letters, 66, 343–345.

[9] P. Verma and A. C. Pandey, (2010), "Organic Capping-Effect and Mechanism in Mn-Doped CdS Nanocomposites," Physica B: Condensed Matter, 405 (5), 1253-1257.

[10] P. Verma and A. C. Pandey, (2011), "Controlled Growth of CdS Nanocrystals: Core/Shell viz Matrix", Journal of Biomaterials and Nanobiotechnology, 2, 409-413.

[11] B.D. Cullity and S.R. Stock, (2001), (2001) "Elements of X-Ray Diffraction (Prentice Hall, Englewood Cliffs, NJ)", 3rd Ed, 167–171.

[12] A.K. Gupta and R. Kripal, (2012), "EPR and photoluminescence properties of Mn^{2+} doped CdS nanoparticles synthesized via co-precipitation method", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 96, 626–631.

[13] M. Sreenivas, G. S. Harish and P. Sreedhara Reddy, (2014), "Synthesis and Characterization of Mn, Ce Co-Doped CDS Nanoparticles Synthesized Via Co-Precipitation Method", International Journal of Modern Engineering Research, 4 (9), 10-16.

[14] N. Romcevic, R. Kostic, M. Romcevic, M.I. Comor and J.M. Nedeljkovic, (2005), "Raman spectroscopy of Cd1-xMnxS quantum dots", Journal of Physics D: Applied Physics, 38, 4321-4324.