International Journal of Theoretical & Applied Sciences, **1**(1): 8-11(2009)

Photo-physical Properties of $Cd_{(1-x)-y}Zn_xFe_yS$ Nanocrystals

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ABSTRACT

Polyvinyl pyrrolidone capped $Cd_{(1-x)-y}Zn_xFe_yS$ [($0\leq x\leq 0.5$); ($0.0001\leq y\leq 0.1$)] nanocrystals have been synthesized using aqueous chemical coprecipitation method. Crystallographic characterization of synthesized quaternary semiconductor compounds have been done using X-ray diffraction (XRD), average crystallite size calculated from the recorded XRD patterns is ~3.5nm. Time resolved luminescence spectra have been recorded using high peak power, pulsed N_2-laser excitation for photo-physical behaviour analysis of synthesized nanocrystals. Decay time values have been calculated from recorded multi-exponential luminescence decay curves using Bube's peeling off method, all the observed decay time values lie in µs time domain. Decay time dependence on dopant concentration has been studied in detail.

Keywords: Nanocrystals, X-ray diffraction, Time resolved spectra, Decay time

INTRODUCTION

Since ancient times intrinsic and extrinsic II-VI chalcogenide and ceramic semiconductors have attracted the interest of researchers due to their wide opto-electronic industrial applications. Photo-physical properties; radiative and non-radiative recombination mechanisms in wide gap semiconductors of II-VI type have been extensively studied over the past 50 years (1-7). After 90's, size dependent tunable properties of semiconductor nanocrystals have attracted the interest of researchers throughout world. Semiconductor nanocrystals are described as a state of matter that is intermediate between individual molecule and bulk (8). Transition from bulk to nanoparticles lead to the display of quantum mechanical properties and an increased dominance of surface atoms, which increases the chemical reactivity of a material. Notable examples include tunable bandgap (9) and catalytic behavior (10), respectively. The small size and high optical activity of certain semiconductors make them interesting for applications in disciplines ranging from Optoelectronics (11), catalysis (12) to fluorescence microscopy (13).

In the present investigation, $Cd_{(1-x)-y}Zn_xFe_yS$ [($0\leq x\leq 0.5$); ($0.0001\leq y\leq 0.1$)] nanocrystals have been synthesized using environment friendly well known bottom-up synthesis technique aqueous chemical coprecipitation method, which has the advantages of producing size-controlled, un-agglomerated nanocrystals. To the best of our knowledge, this is the first report discussing the photo-physical behaviour analysis of iron doped quaternary semiconductor nanocrystals using time resolved laser induced luminescence spectroscopy.

MATERIAL AND METHODS

Synthesis of $Cd_{(1-x)-y}Zn_xFe_yS$ [($0\leq x\leq 0.5$); ($0.0001\leq y\leq 0.1$)] nanocrystals had been carried out using a simple wet chemical coprecipitation method described earlier by Singh et al. (14) for the synthesis of Eu^{3+} doped $Cd_{1-x}Zn_xS$ quantum dots. All synthesis was carried out in water for its inherent advantages of being simple and environment friendly. All steps of the synthesis were performed at room temperature and under ambient conditions. Aqueous solutions of cadmium acetate [$(CH_3COO)_2Cd.2H_2O$], zinc acetate ($C_4H_6O_4Zn.2H_2O$), ferric chloride ($FeCl_3$), sodium sulphide (Na_2SxH_2O) and polyvinyl pyrrolidone (PVP) [$(C_6H_9NO)_n$] were prepared. Then cadmium, zinc and iron precursor solutions were mixed in the stochiometric concentration under vigorous stirring, 4 mL of 2% PVP aqueous solution was added to total 50 mL volume of reaction mixture, before drop wise addition of sulphur precursor. PVP act as the capping agent to avoid the agglomeration of nanocrystals. The resulting precipitates were washed several times with distilled water and dried in vacuum oven for 10-12 hrs.

XRD patterns of the synthesized samples had been recorded using a Panalytical's X'Pert Pro Powder X-ray diffractometer with Cu K_α radiation (λ= 1.541 A°) in the 2θ range 20–60^o. Average crystallite size was calculated from the recorded diffraction patterns using Scherrer formula (15)

$$D = \frac{0.89\lambda}{\beta cos\theta} \qquad \ldots(1)$$

where D is the average crystallite size, λ is incident x-ray wavelength, β is the full width half maximum (FWHM) of diffraction peak expressed in radians and θ is peak position in x-ray diffractogram.

Laser induced time resolved luminescence spectra had been recorded using high peak power (10kW), pulsed N_2-laser (λ=337.1nm) excitation. Decay signals were recorded in the digital storage oscilloscope coupled with PC. Details of the experimental set-up have been already reported by Singh et al (16).

RESULTS AND DISCUSSION

There are many reports dealing with a variety of nanocrystal synthesis techniques. Chemical synthesis of nanoparticles in the form of colloidal solutions, free standing powders or particles embedded in some solid media like glass, polymers, zeolites etc. are well established techniques. In the present investigation a simple colloidal chemical coprecipitation method has been preferred to synthesize $Cd_{(1-x)-y}Zn_xFe_yS$ nanocrystals for a variety of reasons. It is rather simple and inexpensive method in which all steps of synthesis are carried out at room temperature under ambient conditions. All synthesis is carried out in water for its inherent advantages of being simple and environment friendly. The growth mechanism can be explained on the basis of Ostwald ripening (17).

XRD patterns recorded for all the samples show peak broadening due to nanosize formation; one such X-ray diffractogram is shown in Fig. 1. Comparison of the recorded diffraction patterns with JCPDS files reveals that the synthesized nanomaterials exhibit a zinc-blende crystal structure. The three diffraction peaks correspond to (111), (220), and (311) planes of the cubic crystalline CdZnS. XRD analysis show no characteristics peaks of impurity phases. Average crystallite size calculated from the recorded XRD patterns is ~3.5nm.

N_2-laser excitation of $Cd_{(1-x)-y}Zn_xFe_yS$ [(x=0; ($0.0001 \leq y \leq 0.1$)] nanocrystals causes broad emission peaked in green region, which is blue shifted with the addition of zinc due to band gap broadening. Moreover, luminescence quantum efficiency go on decreasing with increasing value of 'y' in $Cd_{(1-x)-y}Zn_xFe_yS$ nanocrystals, due to the reason that photo-excited electrons are transferred to iron metal ion induced trapping states compared to anion vacancy defect centers. Iron ions act as electron trapping centers, which results into non-radiative recombination. Laser induced time resolved luminescence decay curves recorded for all the synthesized samples were multi-exponential due to the transitions between the multi-level trapping states. Fig. 2 shows one such decay curve recorded for $Cd_{(1-x)-y}Zn_xFe_yS$ nanocrystals. Luminescence decay time values have been calculated from recorded multi-exponential decay curves using Bube's peeling-off method. Verma et al. (18) and Bhatti et al. (19) have given the detailed description about the Bube's peeling-off method and hence the calculation of luminescence decay time values. Three values of decay times have been calculated for all the samples due to multi-exponential nature of decay curves. Table 1 shows the room temperature decay time values for synthesized quaternary semiconductor nanocrystals. All the decay time values lie in microsecond time domain ranging from 2.05 to 17.86μs. It is evident from the Table 1 that the decay time values become faster with increasing values of 'x' and 'y' in $Cd_{(1-x)-y}Zn_xFe_yS$. This is due to the band gap broadening with increasing concentration of Zn and increased interaction between the host lattice cations with the dopant ions. But the increased interaction between Fe ions with defect states make the charge of lattice more positive resulting the luminescence quenching. Moreover at higher concentrations clustering of Fe ions results in concentration quenching of luminescence.

CONCLUSIONS

Crystallographic studies of bottom-up grown $Cd_{(1-x)-y}Zn_xFe_yS$ [$(0\leq x\leq 0.5)$; $(0.0001\leq y\leq 0.1)$] nanocrystals reveal zinc blende crystal structure with average crystallite size ~3.5nm. Luminescence quenching with increasing concentration of Fe ions and decay time shortening with increasing 'x' and 'y' values in $Cd_{(1-x)-y}Zn_xFe_yS$ nanocrystals have been observed. Decay time dependence on dopant concentration reported in the present investigation will be very beneficial for the nanophosphor calibration curves.

ACKNOWLEDGMENTS

Authors are grateful to RSIC, Punjab University, Chandigarh and especially Mr. Jagtar Singh for crystallographic studies.

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Fig. 1. XRD pattern of $Cd_{(1-x)-y}Zn_xFe_yS$ nanocrystals

Fig. 2. Decay curve for $Cd_{(1-x)-y}Zn_xFe_yS$ nanocrystals

Table1. Room temperature luminescence decay time values for $Cd_{(1-x)-y}Zn_xFe_yS$ nanocrystals

Sr. No.	Sample	Decay time (μs)		
		τ_1	τ_2	τ_3
1.	$CdS:Fe^{2+}$ (0.01%)	2.89	5.92	17.86
2.	$CdS:Fe^{2+}$ (0.10%)	2.82	5.74	17.43
3.	$CdS:Fe^{2+}$ (1.00%)	2.76	5.62	16.97
4.	$CdS:Fe^{2+}$ (10.00%)	2.68	5.45	16.54
5.	$Cd_{0.9}Zn_{0.1}S:Fe^{2+}$ (0.01%)	2.78	5.68	17.12
6.	$Cd_{0.9}Zn_{0.1}S:Fe^{2+}$ (0.10%)	2.71	5.53	16.69
7.	$Cd_{0.9}Zn_{0.1}S:Fe^{2+}$ (1.00%)	2.64	5.39	16.35
8.	$Cd_{0.9}Zn_{0.1}S:Fe^{2+}$(10.00%)	2.55	5.26	15.92
9.	$Cd_{0.7}Zn_{0.3}S:Fe^{2+}$ (0.01%)	2.62	5.33	16.08
10.	$Cd_{0.7}Zn_{0.3}S:Fe^{2+}$ (0.10%)	2.54	5.17	15.73
11.	$Cd_{0.7}Zn_{0.3}S:Fe^{2+}$ (1.00%)	2.43	4.98	15.04
12.	$Cd_{0.7}Zn_{0.3}S:Fe^{2+}$(10.00%)	2.32	4.76	14.44
13.	$Cd_{0.5}Zn_{0.5}S:Fe^{2+}$ (0.01%)	2.38	4.90	14.88
14.	$Cd_{0.5}Zn_{0.5}S:Fe^{2+}$ (0.10%)	2.29	4.68	14.20
15.	$Cd_{0.5}Zn_{0.5}S:Fe^{2+}$ (1.00%)	2.18	4.45	13.49
16.	$Cd_{0.5}Zn_{0.5}S:Fe^{2+}$(10.00%)	2.05	4.22	12.78