Asian Journal of Chemistry Vol. 18, No. 5 (2006), 3295-3300

Synthesis and Time Resolved Laser Spectroscopy of CdS Nanophosphors

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Pure and transition metal doped CdS nanophosphors have been synthesized using chemical precipitation method. Time resolved spectra of these synthesized phosphors have been recorded using high peak power, pulsed N_2-laser as excitation source. Oscillator strength and dipole-moment values have been calculated from the recorded spectra. X-ray diffraction (XRD) technique has been used for the morphological characterization of synthesized materials. Average crystallite size has been calculated from the XRD patterns by using Scherrer's formula.

Key Words: CdS nanophosphors, Time resolved spectra, Oscillator strength, Dipole-moment.

INTRODUCTION

In recent years, synthesis and characterization of semiconductor nanoparticles have attracted much interest because of their novel properties as a consequence of the large number of surface atoms and three-dimensional confinement of the electrons[1]. There are extensive studies on optical responses of semiconductor nanocrystals because these exhibit a wealth of quantum phenomena and their size–dependent optical properties open new applications including displays and optoelectronic devices[2-3]. Nanostructured materials especially II-VI semiconductors have become a subject of intensive research for their extraordinary properties compared to their bulk counterparts[4]. Blue shift of the optical absorption spectrum, size dependent luminescence, enhanced oscillator strength, nonlinear optical effect are some examples of the interesting properties exhibited by these nanoparticles. Particularly, semiconducting materials in nanostructured form offers the possibility of possessing large optical nonlinear susceptibility and ultra fast response[5,6]. Also these are very attractive for the realization of thermally stable and frequency selective lasers and photodetectors[7], whose performance have been found to be modulated drastically by shape and sizes of the nanocrystallites. Moreover, among a variety of semiconductor materials, the binary metal chalcogenides of group II have been extensively studied. For example, nanocrystalline CdS and ZnS are attractive materials in photoconducting cells and optoelectronic devices such as solar cells and photodetectors[8,9]. Also, the related ternary compounds $Cd_xZn_{1-x}S$ are promising materials for high-density optical recording and laser diodes.

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In present paper, CdS and $Cd_xZn_{1-x}S$ ($0.4 \leq x \leq 1$) nanoparticles have been synthesized at room temperature by using well-known bottom-up synthesis technique chemical precipitation method. Time resolved photoluminescence spectra of these synthesized nanoparticles have been recorded by using high peak power, pulsed UV N_2-laser as excitation source. Green and red emissions have been observed from the nanophosphors. Important optical parameters like oscillator strength and dipole-moment values have been calculated from the recorded PL spectra with the help of computer simulations. X-ray diffraction (XRD) studies have been carried out for nano size confirmation and characterization of synthesized phosphor materials.

EXPERIMENTAL

Sample preparation

Pure and Zn doped CdS nanophosphors have synthesized at room temperature using chemical precipitation method[10]. These nanophosphors have been synthesized from cadmium acetate dihydrate, thiourea, zinc acetate dihydrate and ammonia solution. 0.5M aqueous solution of cadmium acetate dihydrate, thiourea and zinc acetate dihydrate have been prepared in three different beakers. These three solutions have been mixed in the stochiometric concentration, pH of the resulting mixture is kept fixed at 10.5 with dropwise addition of ammonia solution. The resulting precipitates are filtered and dried in vacuum oven.

Morphological characterization and nanosize confirmation

XRD patterns for the synthesized phosphor samples have been recorded using Philips PW 1710 powder X-ray diffractometer with Cu K_α radiation (λ=1.541 A^0) in 2θ range 20-60^0. Average crystallite size has been calculated from the recorded XRD patterns using well known Scherrer formula[11].

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

Where D is the average crystallite size, B is the full width half maximum (FWHM) of X-ray diffraction peak expressed in radian and θ is the position of the diffraction peak in the diffractogram.

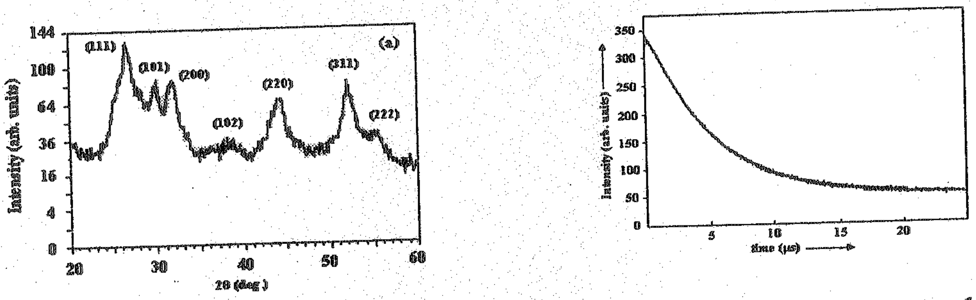

Fig. 1. (a) XRD pattern (b) Hyperbolic decay curve recorded for $Cd_{0.60}Zn_{0.40}S$ nanophosphors

Photoluminescence studies

High peak power (10 kW), pulsed (< 10 ns) N_2-laser (337.1 nm) has been employed as an excitation source for luminescence studies. Short lived phosphorescence from the samples has been recorded on digital storage oscilloscope through an assembly of glass slab (UV radiation filter) monochromator (wavelength selective element) and photomultiplier tube (transducer). The recorded PL decay curves are hyperbolic in nature and have been peeled-off into three components using peeling-off method of Bube using computer simulations[12]. When samples are exposed to high energy radiations, the electrons are raised from the valence band to the excited states. On returning back to the valence band, there is emission of energy. The intensity of the luminescent radiation at any time, t, is given by

$$I = I_o e^{-pt} \tag{2}$$

where I_o is the intensity of the radiation at cut-off position and the constant p is the transition probability of the corresponding radiative transition. Constant 'p' gives value of transition probability. A plot of ln I *vs.* t will be a straight line in case of single set of traps. However, in most of the cases, when one goes across the interaction of radiation with solids, there are trapping levels at different depths leading to multiple transition probability components from nonlinear plot of ln I *vs.* t.

The electromagnetic radiations interact with an electronic centre through the electric or magnetic fields of the radiation. The oscillator strength 'f' of a transition is a dimensionless quantity that is useful for comparing different radiative transitions. The oscillator strength of electric dipole allowed transitions[12,13] is given by the relation:

$$f_{ed}(v) = 1.5\times10^4 \lambda^2 \frac{9}{(n^2+2)^2 n} p \tag{3}$$

where λ is emission wavelength, n is the index of refraction, p is the transition probability. For magnetic dipole transitions the above relation reduces to

$$f_{md}(v) = 1.5 \times 10^4 \lambda^2 \frac{1}{n^3} p \qquad (4)$$

An electric dipole transition will have a lifetime of 10^{-8} to 10^{-7} s, while a magnetic dipole transition 10^{-3} to 10^{-1} s and a quadruple transition have even longer lifetime. Eq. 3 has been used to calculate the oscillator strengths of weak electric dipole transitions.

The corresponding dipole-moment[12,13] is given by the relation:

$$|\mu| = (\frac{3h\varepsilon_o\lambda^3}{16\pi^3 n} p)^{\frac{1}{2}} \qquad (5)$$

where h is Planck's constant, ε_0 is the absolute permittivity of free space, λ is emission wavelength, p is the transition probability

RESULTS AND DISCUSSION

Comparison of the recorded diffractogram shown in Fig. 1(a) with standard JCPDS data base files JCPDS 80-0019 and JCPDS 08-0006 have confirmed the biphase existence. Both zinc blende structure with lattice parameter a = 0.5832 nm and wurtzite structure having lattice parameters a = 0.4160 nm and c = 0.6756 nm show their existence in synthesized nanophosphors. Crystallite size of synthesized phosphors is < 10 nm. Decay curves are hyperbolic in nature as shown in Fig. 2(a) Three values of oscillator strength and dipole-moment have been calculated for each sample for each emission colour as shown in Table 1 and 2. Both Oscillator strength and dipole-moment values increase with increasing atomic concentration of Zn in CdS. Both of these values are more for red emission in comparison to green emission. In case of green emission oscillator strength and dipole-moment have maximum values 32.2824×10^{-6} and 5.7047×10^{-31} cm, respectively for $Cd_{0.60}Zn_{0.40}S$ and minimum values 3.5460×10^{-6} and 1.8906×10^{-31} cm, respectively for CdS, whereas for red emission maximum values are 46.0617×10^{-6} and 7.5982×10^{-31} cm, respectively for $Cd_{0.60}Zn_{0.40}S$ and minimum values 2.9948×10^{-6} and 1.9375×10^{-31} cm, respectively for pure CdS.

Conclusion

Dipoles get aligned and strength of transitions increases with increasing atomic concentration of Zn in CdS nanophosphors. Moreover, bond strength increases and electric dipole interactions become dominant over the magnetic dipole interactions. So probability of radiative transitions increase.

TABLE- 1
OSCILLATOR STRENGTH VALUES FOR $Cd_XZn_{1-X}S$ RECORDED AT ROOM TEMPERATURE FOR GREEN AND RED EMISSION

S. No.	Sample	Oscillator strength values for green emission (x 10^{-6})			Oscillator strength values for red emission (x 10^{-6})		
		f_1	f_2	f_3	f_1'	f_2'	f_3'
1.	CdS	14.8366	7.2682	3.5460	18.8171	10.1082	2.9948
2.	$Cd_{0.95}Zn_{0.05}S$	17.8608	7.9206	3.7218	23.9090	12.9457	3.8099
3.	$Cd_{0.90}Zn_{0.10}S$	18.3562	8.8022	3.8731	24.7303	13.1783	4.1208
4.	$Cd_{0.85}Zn_{0.15}S$	19.4644	10.3108	4.0237	25.1137	14.7705	4.1987
5.	$Cd_{0.80}Zn_{0.20}S$	24.1343	14.0806	4.0864	36.1638	20.1744	5.0925
6.	$Cd_{0.75}Zn_{0.25}S$	25.7400	16.0998	4.3509	37.4528	20.7671	5.7145
7.	$Cd_{0.70}Zn_{0.30}S$	26.5835	16.9804	4.7032	41.2697	20.9236	6.4152
8.	$Cd_{0.65}Zn_{0.35}S$	29.9024	18.1051	5.3540	43.0998	22.7878	6.5316
9.	$Cd_{0.60}Zn_{0.40}S$	32.2824	18.6143	6.7894	46.0617	26.8666	6.8036

TABLE- 2
DIPOLE-MOMENT VALUES FOR $Cd_XZn_{1-X}S$ RECORDED AT ROOM TEMPERATURE FOR GREEN AND RED EMISSION

S. No.	Sample	Dipole-moment values for green emission (x 10^{-31} cm)			Dipole-moment values for red emission (x 10^{-31} cm)		
		μ_1	μ_2	μ_3	μ_1'	μ_2'	μ_3'
1.	CdS	3.8674	2.7068	1.8906	4.8564	3.5594	1.9375
2.	$Cd_{0.95}Zn_{0.05}S$	4.2432	2.8257	1.9369	5.4742	4.0281	2.1852
3.	$Cd_{0.90}Zn_{0.10}S$	4.3017	2.9788	1.9759	5.5675	4.0642	2.2727
4.	$Cd_{0.85}Zn_{0.15}S$	4.4296	3.2240	2.0140	5.6104	4.3027	2.2940
5.	$Cd_{0.80}Zn_{0.20}S$	4.9325	3.7675	2.0297	6.7325	5.0285	2.5264
6.	$Cd_{0.75}Zn_{0.25}S$	5.0939	4.0286	2.0943	6.8515	5.1019	2.6763
7.	$Cd_{0.70}Zn_{0.30}S$	5.1767	4.1373	2.1774	7.1921	5.1211	2.8356
8.	$Cd_{0.65}Zn_{0.35}S$	5.4904	4.2722	2.3232	7.3499	5.3444	2.8612
9.	$Cd_{0.60}Zn_{0.40}S$	5.7047	4.3318	2.6162	7.5982	5.8029	2.9202

ACKNOWLEDGMENTS

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

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