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EFFECT OF TEMPERATURE ON THE SYNTHESIS OF CdS:Mn DOPED NANOPARTICLES

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The present paper reports the synthesis and the characterization of luminescent CdS:Mn doped nanoparticles of different sizes by chemical route in the presence of the capping agent, thioglycerol. Nanoparticles of CdS:Mn were synthesized at different temperatures. The particle size of such samples were measured using XRD pattern and was found to be in between 2nm - 4nm.The particle size was also calculated from two theoretical models, and was found between 1.5nm-3.8nm.on the basis of absorption spectra.The blue-shift in absorption spectra was obtained with reducing size of the nanoparticles. It was observed that the particle size decreases with decreasing synthesis temperature.

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1. Introduction

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor nanoparticles, surface plasmon resonance in some metal particles and super para magnetism in magnetic materials. The properties of materials change as their size approaches the nanoscale and the percentage of atoms at the surface of a material becomes significant. Modification in the electronic levels occurred very strongly due to the limited number of atoms in the particles. Such materials in these regime exhibit novel physical and chemical properties due to the large surface to volume ratio as well as size quantization effect in semiconductor nanoparticles [1-4]. Due to finite size of the nanoparticles the continuous energy band of the bulk crystal transforms into a series of discrete states resulting in widening of the effective band gap. The nanoparticles frequently display photoluminescence and sometimes display electroluminescence [5-10]. Additionally, some nanoparticles can form self-assembled arrays [11-12]. Because of these favorable properties, nanoparticles are being extensively displays studied for use in optoelectronic.

Doped semiconductor are extensively investigated to obtain basic information on impurity states in quantum dots and to examine their potential applications in novel light-emitting devices. It is well known that the quantum confinement effect modifies the electronic structure of nanocrystals when their diameter is comparable to or smaller than the diameter of the bulk exciton [13-15]. Moreover, recent results on ZnS:Mn nanocrystals show that the position of the Mn^{2+} emission band is slightly shifted from that of the bulk material[16].

The synthesis of semiconductor nanoparticles (NPs) has attracted many researchers, due to their unique optoelectronic properties and quantum confinement effects from the bulk materials

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[17-19]. In the present work CdS:Mn doped nanoparticles of different sizes have been synthesized by chemical route method at different temperatures and for various concentration of capping agents, and their optical absorption spectra and XRD have been investigated. This work could also provide important information about the trap emission in CdS:Mn doped nanoparticles.

2. Experimental

Nanoparticles of manganese doped cadmium sulphide are prepared by wet chemical route method. For synthesis, 10^{-2} M aqueous solution of $CdCl_2$, thioglycerol [$C_3H_8O_2S$] and Na_2S solutions were prepared. Firstly, thioglycerol solution was added drop wise to $CdCl_2$ (+$MnCl_2$ for doping) solution at the rate of 1ml per minute, while stirring it continuously so that solution are mixed properly. Then Na_2S solution will be added in a similar manner. The chemical reaction gives CdS.

$$CdCl_2 + Na_2S \rightarrow CdS + NaCl$$

The precipitate of CdS is insoluble in water and were thoroughly washed in double distilled water, centrifuged and then air dried. The presence of thioglycerol does not allow the particle size to grow in bigger size. Three different samples were prepared at 0° c, room temperature and at 70° c for fixed concentration of Mn (0.8%). Similar method is used to prepare the samples of CdS:Mn for 10^{-1}M and 1M concentrations of the capping agents.

All the samples were characterized at Inter University Consortium (IUC) Indore for X-ray diffraction studies with Cu Kα radiation (λ=1.5418 Å). XRD data were collected over the range 20^0-70^0 at room temperature.X-ray diffraction patterns have been obtained by Rigaku Rotating Anode (H-3R) diffractometer. The particle size was calculated using the Debye-Scherrer formula.

Absorption spectra of the samples prepared with various concentrations of capping agent and at different tempreture were studied. The absorption spectra of the samples were recorded with the help of Shimadzu UV/VIS- 1700 spectrophotometer.

3. Results and discussion

The XRD patterns of the samples are shown in Figure 1. Three different peaks are obtained at 2Θ values of 26.74 °, 43.86° and 51.64 °. This shows that the samples have zinc blende structure. The XRD peaks correspond to Bragg diffraction at (111), (220) and (311) planes of cubic CdS. The broaden peaks indicates nanocrystalline behavior of the CdS sample. The width of the peak increases as the size of the particle decreases. The size of the particles has been computed from the full width half maximum (FWHM) of the first peak using Debye Scherer formula [20].The particle size of all the samples are in the range 2nm-4nm.

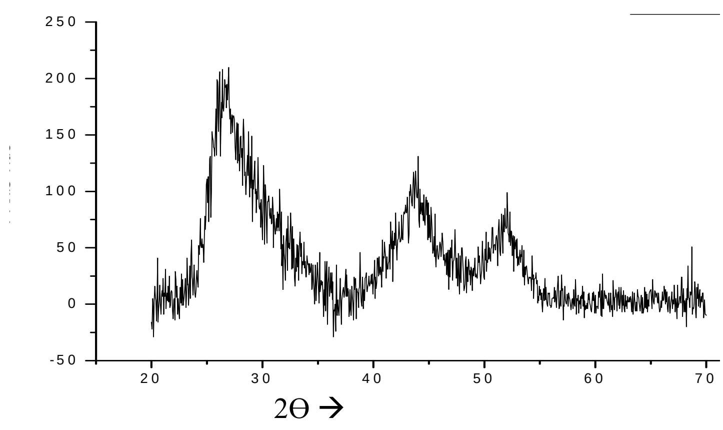


Fig. 1 XRD pattern of CdS:Mn nanoparticle.

Figure 2(a) shows the optical absorption spectra of CdS:Mn nanoparticles with three molar concentration 1M, 10^{-1}M and 10^{-2}M of thioglycerol. It was found that with increasing concentration of capping agent the optical edge shifts towards the lesser value of wave length. The observed blue shift in the absorption edge is the reflection of increase in the band gap owing to quantum confinement effect. Band gap of standard material of CdS (bulk) is 2.4 eV, but the band gap of synthesized CdS (bulk) in lab was 2.26 eV on the basis of absorption spectra. The band gap energy of the samples synthesized at 0^{o}c temperature corresponding to the absorption edge is found in the range 2.6eV- 2.88eV with increasing the capping agent concentration.

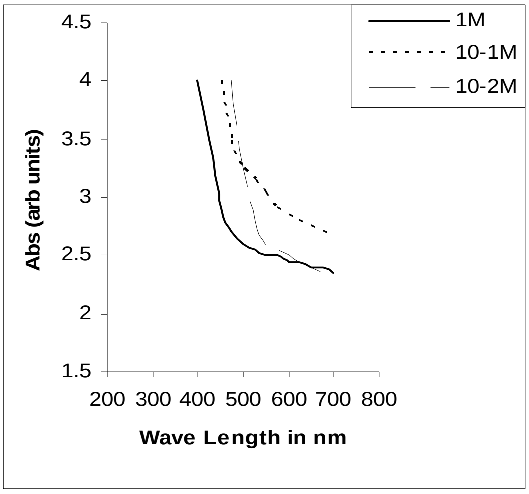


Fig. 2(a) Optical absorption spectra of CdS:Mn for diff. molar concentration of capping agent synthesized at 0^{o} C.

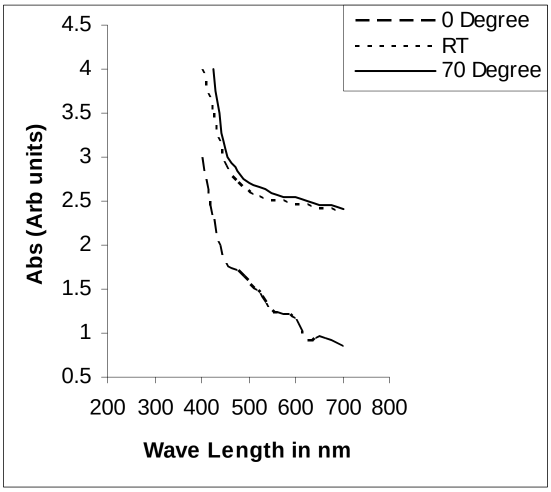


Fig. 2(b) Optical absorption spectra of CdS:Mn for 1Mole Cocentration synthesized at different temperatures.

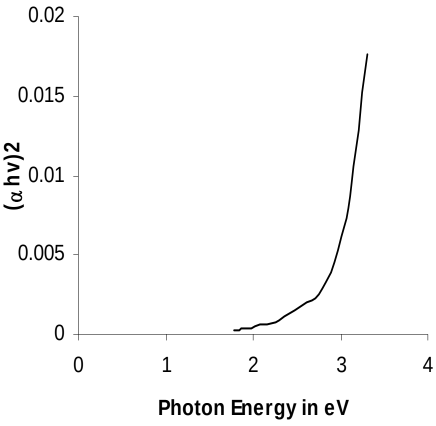
Figure 2(b) shows the optical absorption spectra of CdS:Mn doped nanoparticles synthesized at various temperature for 1mole concentration of capping agent. It was observed that a systematic shift in the absorption edge occurs, as the synthesis temperature is lowered. The absorption edge shifts towards the shorter wave length side. It is more for the sample synthesized at 0^{o}c. So the size of the nanoparticles decreases with decreasing synthesis temperature. Thus, due to the quantum confinement effect, more discrete energy states are formed, resulting in widening of the band gap of the nanoparticles [21].

The most accurate model for determining the electronic structure of II–VI nanocrystals is the tight-binding approximation with the sp^3d^5 orbital basis and next nearest neighbor interactions between the anions and the cations [22-23]. Here two theoretical models are used for calculating the size of the nanoparticles which relates the variation of band gap with particle size. (i) Effective Mass Approximation (EMA) and (ii) Hyperbolic Band Model (HBM). The size of the samples calculated by both model is likely to be equal. We attribute it to the fact that the temperature used (0°C) for synthesizing the sample gives a rather large size distribution. The band gap energy of the samples corresponding to the absorption edge is found in the range 2.6 eV- 2.88 eV.

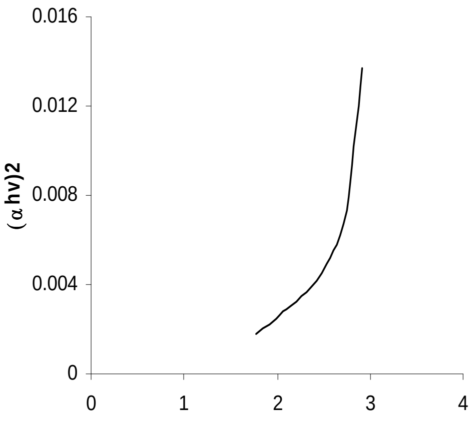
Table 1

S. N.	Synthesis Temp.	Concentration of capping agent	Absorption edge λ(nm)	Eg. confineme-nt (eV)	EMA (nm)	Hyperbolic (nm)
1.	70^0 C	10^0	431	2.62	2.038	3.831
2.	30^0 C	10^0	460	2.7	1.843	3.666
3.	0^0 C	10^0	431	2.88	1.553	3.350
4.	0^0 C	10^{-1}	440	2.82	1.634	3.446
5.	0^0 C	10^{-2}	475	2.60	2.067	3.853

Table1 shows the optical absorption edge, confinement energy, and particle size calculated by two different theoretical models at three different temperatures, when the concentration of capping agent was kept constant. It also shows that the particle size changes with the change in the molar concentration of the capping agent when the synthesis temperature was not changed. It was found that the particle size decreases with increase in the concentration of the capping agent The particle size of the samples is in the same range as obtained by XRD i.e. 1.5nm-3nm approximately.



Taus plot of CdS:MnNano at 0⁰C for 1M cocen.



Taus Plot for CdS:Mn Nano at 70⁰C 1M concen.

Fig. 3. The plot between $(\alpha h\nu)^2$ verses energy ($h\nu$) of CdS:Mn nanoparticles

Figure 3 shows the plot between $(\alpha h\nu)^2$ verses energy ($h\nu$) of CdS:Mn doped nanoparticles synthesis at 0˚c and 70˚c for 1M concentration of capping agent. It is seen from the plot that the band gap energy of the samples increases with decreasing synthesis temperature of the samples.

4. Conclusion

The nanoparticles of CdS:Mn were grown by chemical routs at different temperature such as 0 ˚C, room temperature and 70 ^{o}C in which thioglycerol was used as the capping agent . The XRD pattern indicated the growth of the nanoparticles. The blue shift in the absorption spectra and the calculation of particle size by the measurement of absorption edge from two theoretical models indicates the reduction in particle size with the increase in the molar concentration of the capping agents. The size of the nanoparticles decreases as the reaction temperature is decreased. So, the temperature is also an important parameter for the synthesis of CdS:Mn doped nanoparticles.

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