THERMOLUMINESCENCE AND OPTICAL ABSORPTION SPECTRA OF ZnS:Mn NANOPARTICLES

RAVI SHARMA[a*], B.P.CHANDRA[b], D.P.BISEN[c]

[a]*Department of Physics, Arts & Commerce Girls College, Devendra Nagar Raipur (C.G.) 492001*
[b]*Department of Applied Physics,Shri Shankaracharya College of Engineering & Technology,*
[c] *School of studies in Physics, Pt. Ravishankar Shukla University, Raipur(C.G.) 492010*

ZnS:Mn nanocrystals show a high luminescence quantum efficiency, and,therefore,they have potential for their use in several opto-electronic devices The present paper reports the synthesis and characterization of luminescent nanocrystals of manganese doped zinc sulphide ,which were prepared by chemical deposition method using the solution of zinc chloride ,sodium sulphide and manganese chloride, whereas mercaptoethanol was used as an capping agent .The particle size of such nanocrystals was measured using XRD pattern and it is found to be in between 3nm - 4nm. The optical absorption spectra of the samples shows the blue-shift with decreasing particle size .. The thermoluminescence (TL) of ZnS:Mn nanoparticles is also reported. The TL intensity increases as the particle size is decreased. The shift in peak position was also seen with decreasing size.The consistency of the size dependence of the TL with that of the surface fluorescence indicates that the TL may be related to the surface states.

1. Introduction

Materials with nanoscopic dimensions such as quantum dots, nanowires, nanorods and nanotubes, have attracted a great deal of attention during the last four decades [1,2]. This is due to their intriguing properties that cannot be obtained from the conventional macroscopic materials. Nanophosphors material are of potential interest in non-linear optics and in fast optical switching [3-4].Quantum dots of II-VI semiconductors have attracted particular attention because they are easy to synthesize in the size range required for quantum confinement. The crystallinity, melting point and structural stability are strongly influenced by the reduction of the particle size. The change in the properties of nanoparticles is driven mainly by two factors, namely the increase in the surface to volume ratio and the change in electronic structure of the material due to quantum confinement effect. As the particles become smaller, the surface/volume ratio and the surface states increase and therefore reduce the excited emission via nonradiative surface recombination. This indicates that the surface states are very important to the physical properties, especially the optical properties, of nanoparticles. The study of the surface states or trapping states is not less important as the design for the quantum confinement[5]. As the fluorescence quantum efficiency of nanoparticles is quite low, sensitive means are needed for the luminescence measurement and to study the surface behavior. Thermoluminescence (TL) is a very sensitive technique for the detection of traps or defects.

Semiconducting nanomaterials have attracted growing interest recently due to their unique optical and, transport properties which are potentially useful for technological applications like indicators, analysis of water pollution, environmental studies, pathological investigations, etc. ZnS is semiconducting materials, which has a wide band gap of 3.70eV [6, 7]. It is a well studied material for its luminescence characteristics and particularly for their lifetime shortening and enhanced emission efficiencies [8,9].There   are different methods for synthesis and characterization of nanometer- sized semiconductors. In this work zinc sulfide nanocrystals are prepared by chemical deposition method in which mercaptoethanol has been used for capping, which modifies surface of nanoparticles and prevents the growth of the particles to larger size. The ZnS phosphors are also doped with the Mn .The present paper reports the preparation, characterization, thermoluminescence and absorption of nanoparticles.

2. Experimental

The powder of ZnS nanoparticles were prepared by using chemical deposition technique described by Khosravi [10]. For synthesis, the 1M aqueous solution of $ZnCl_2$ and 1M aqueous solution of Na_2S were mixed in the presence of various concentration of mercaptoethenol solution. $MnCl_2$ was also mixed in the solution in ratio 99:1, while stirring the solution continuously. The obtained precipitate was washed thoroughly three to four times with double distilled water and then separated by centrifuge at 3500 rpm, and finally air-dried. Special care has to be taken to maintain the same physical condition during the synthesis of the sample.

The morphologies and sizes of the mercaptoethanol capped ZnS:Mn were determined by X-ray diffraction studies with Cu Kα radiation (λ=1.5418 Å). XRD data were collected over the range 20^0-80^0 at room temperature.X-ray diffraction patterns have been obtained by Rigaku Rotating Anode (H-3R) diffractometer at IUC,Indore. The particle size was determined using the Debye-Scherrer formula.

The thermoluminescence was recorded by using TLD reader in which heating rate was 560^0C/min.

The optical absorption spectra of the samples prepared with various concentrations of capping agent were studied. The Perkin Elmer,USA Lamda 950 model UV-VIS spectrometer is used to obtain the optical absorption spectra of ZnS:Mn nanoparticle. Data was collected in absorbance mode from 200 to 400 nm range.

3. Results and discussion

The XRD patterns for the samples are shown in Fig. 1.Three different peaks are obtained at 2Θ values of 29.50 °, 48.80° and 57.80 °. This shows that the samples have zinc blende structure and the peaks correspond to diffraction at (111),(220) and (311) planes, respectively [11]. The lattice parameter has been computed as 5.31 Å, which is very close to the standard value (5.42 Å). It is also seen from the Fig 1 that peaks are broadened for higher concentration of capping agent. The broadening of peaks indicates nanocrystalline behavior of the particles. The size of the particles has been computed from the width of first peak using Debye Scherrer formula [12]:
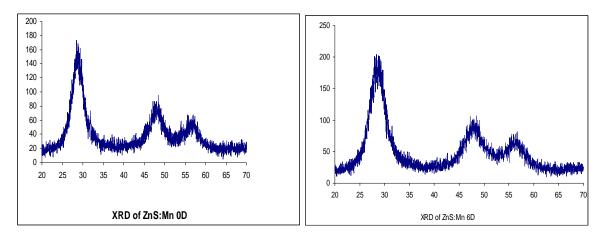
Fig.1. XRD pattern of ZnS : Mn

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where K is constant (K=.9), λ is the wavelength of X-rays, β is the full width at half maximum and Θ is Bragg angle. The particle sizes obtained from XRD are of the order of 3-4 nm.
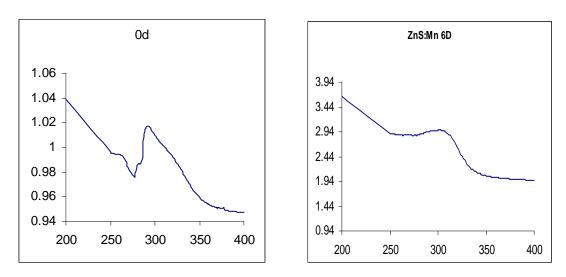

Fig. 2: Optical absorption spectra of ZnS : Mn

Fig 2 shows the optical absorption spectra of ZnS nanoparticles in the range of 400nm-200 nm. It is seen that the spectra are featureless and no absorption occur in visible region(800 nm-390nm). Absorption edge was obtained at shorter wavelength in UV region at 280 nm, 260 nm, for ZnS0, ZnS6 samples, respectively. This clearly shows that the absorption edge shift towards shorter wavelengths as the capping agent concentration is increased. The observed blue-shift in the absorption edge is reflection of the band gap increase owing to quantum confinement effect. In the bulk material the band gap can be found from the graph between $(\alpha h\nu^2)$ vs. $h\nu$ whereas in the nanomaterials the band gap is obtained from the absorption maxima. The absorption edge was found at shorter wavelength. The band gap energy of the samples corresponding to the absorption edge is found in the range 4.5eV- 5.1eV with increasing the capping agent concentration. Similar results are reported by Kumbhojkar *et al.*[13] on mercaptoethanol capped ZnS nanoparticles.
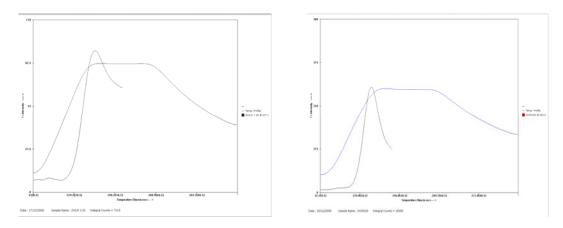
Fig. 3:   The TL spectra of ZnS : Mn

Figure 3 shows the glow curves of the nanoparticles. It is seen thatthe glow peak occurs around 380 K from the nanoparticles. Both the samples show the glow peaks at different position and the TL intensity increases as the particles size is decreased. Similar results were reported by Chen et . al .[14]. The change of TL is consistent with that of the surface fluorescence. It is reasonable to consider that the TL of the nanoparticles is correlated to the surface state The glow peaks in Fig. 3 are caused by the trapped carriers which are produced during the sample processing. As the particles become smaller, ions at the surface increase rapidly. In nanoparticles, most ions at the surface are not saturated in coordination, electrons or holes may be excited easily and escape from the ions, and then they are trapped at surface states located in the forbidden gap. When the sample is heated the detrapping of electrons and their subsequent recombination with holes gives rise to the light emission.

4. Conclusions

The nanoparticles of ZnS:Mn were grown by chemical routs in which mercaptoethanol was used as capping agent . The size of nanoparticle was found to decrease with increasing concentration of mercaptoethanol. The XRD pattern indicated the growth of the nanoparticles. The measurement of optical absorption spectra indicated blue-shift with reducing size of the nanoparticles.The measurement of TL glow curve suggests the trapping of electrons during the growth of nanoparticles and therefore non-irradiated nanoparticles exhibit TL . The peak position and the peak intensity depends upon the size of the nanaoparticles .

References

[1] Peng, W.Q.; Cong, G.W.; Qu, S.C.; Wang, Z.G. Opt. Mater. **29**, 313,(2006).

[2] Bouvy, C.; Piret, F.; Marine, W.; Su, B.L. Chem. Phys. Lett.**433**, 350,(2007).

[3] T.S. Phely-Bobin, R.J.Muisener, J.T. Koberstein,F.Papadimitrakopoulos, Synth.Met. **116**, 439 (2001).

[4] R..J.Bandaranayake, G.W.Wen, J.Y.Lin,H.K.JiangandC.M.Sorensen, Appl.Phys.Lett. **67**, 831(1995).

[5] M. Tomita and M. Matsuoka, J. Opt. Soc. Am. B **7**, 1198 (1990).

[6] D.Denzler, M.Olschewski, K.Sattler, J.Appl.Phys. **84**, 2841 (1998).

[7] Zou B S,Little R B,Wang J P and E L-Sayed M A Int .J. Quantum Chem.**72**,439 (1999).

[8] R.N.Bhargava and D.Gallangher, Phys.Rev.Lett **72**,416 (1994).

[9] T.Igarashi, T.Isobe, and M.Senna, Phys.Rev.B **56**, 6444 (1995).

[10] A.A. Khosravi, M.Kundu, G.S.Shekhawat, R.R.Gupta, A.K.Sharma, P.D.Vyas, S.K.Kulkarni, Appl. Phys. Lett. **67**, 2506 (1995)

[11] Mahamuni, S.; Khosravi, A.A.; Kundu, M.; Kshirsagar, A.; Bedekar,A.; Avasare, D.B.; Singh, P.; Kulkarni, S.K. J. Appl. Phys.,**73**, 5237, (1993).

[12] Guinier, A. X-ray Diffraction, Freeman, San Francisco (1963).

[13] Kumbhojkar, N.; Nikesh, V.V.; Kshirsagar, A.; Mahamuni, S. J. Appl. Phys., **88**, 6260,(1999).

[14] Wei Chen,a) Zhanguo Wang, Zhaojun Lin, and Lanying Lin , Appl. Phys. Lett. **70**, (1997)