Effect of ZnS nanoparticles on the photoluminescence of Sm$^{3+}$ ions in methanol

D Kakoti$^1$, N Rajkonwar$^1$, N Dehingia$^1$, A Boruah$^1$, P Gogoi$^2$ and *P Dutta$^1$

$^1$Laser and Spectroscopy Laboratory, Department of Physics, Dibrugarh University 786004, Dibrugarh, Assam, India.
$^2$Dibrugarh University Institute of Engineering and Technology, 786004 Dibrugarh, Assam, India.

*pankaj@dibru.ac.in

Abstract: ZnS nanoparticles co-doped with Sm$^{3+}$ ions were prepared in methanol medium for fixed Sm$^{3+}$ and varying ZnS concentrations. Enhancements in absorption as well as photoluminescence efficiency of the co-doped samples were observed. This enhanced efficiency is attributed to the effective increase in oscillator strengths of the Sm$^{3+}$ transitions because of the addition of ZnS nanoparticles.

Keywords: Semiconductor nanoparticles, rare earth, photoluminescence, energy transfer.

1. Introduction

The photoluminescence (PL) properties of rare-earth (RE) elements have been a vast area of research for a few decades. An attractive feature of REs is their sharp and stable emission which depends strictly on the tri-positive RE ion and to some extent on the environment or host [1]. The Sm$^{3+}$ ion is one of the important RE ions which exhibits intense PL in the visible region. It finds wide applications in high-density optical storage, under sea communications, colour displays and visible solid-state lasers [2]. The application domains of Sm$^{3+}$ mainly depend on its emission characteristics. Hence there is a need of enhancing the emission efficiency of Sm$^{3+}$ in different hosts. One potential way of enhancement of the emission efficiency is by sensitization of the Sm$^{3+}$ ions with different entities viz. nanoparticles (NP), ligands, other REs etc. Semiconductor NPs possess very good potential in the area of sensitized luminescence because the band gap energy of the semiconductor NP is of the order of the emission energy of the RE ions. Also, since the absorption cross section of the semiconductor NPs is quite high in comparison to the RE ions, they can absorb excitation energy from the source and can sensitize the RE ions by the recombination of the electron hole pairs [3, 4]. ZnS NPs have been extensively studied due to their outstanding optical properties. These are promising materials for absorption and emission in UV and visible (VIS) regions [5]. Nanosized ZnS exhibits discrete electron energy levels with high oscillator strength and strong luminescence due to the well known quantum confinement effects. Hence it bears potential as effective sensitizer for tri-positive RE ions [6]. The PL enhancement of Eu$^{3+}$ due to the energy transfer from ZnS to Eu$^{3+}$ in ZnS:Eu$^{3+}$ nanocrystal has been reported by Sun et al. [7]. Chen et al. have studied the energy transfer from ZnS to Tb$^{3+}$ with the help of absorption, excitation and PL of ZnS/ Tb$^{3+}$ in water, isooctane microemulsion and sodium bis
sulfosuccinate [8]. ZnS doped with Sm$^{3+}$ is reported to be a good red emitter in thin film electroluminescence devices by T. Tohda et al [9].

In this present work we report the effect of ZnS NPs on the enhancement of PL efficiency of Sm$^{3+}$ ions in methanol.

2. Experimental

At first the ZnS NPs were prepared in DMSO by mixing zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O, Loba Chemie, 96.103%) in dimethyl sulfoxide (DMSO, SRL 99%). The mixture was then heated to 60°C and kept at that temperature for five hours. The resultant solution became whitish signifying the formation of ZnS NPs. Stock solution of Samarium was prepared by dissolving Samarium nitrate hexahydrate (Sm(NO$_3$)$_3$.6H$_2$O, Sigma Aldrich, 99.9%) in 2 ml methanol and magnetically stirring for 15 minutes. The two solutions were then mixed and further stirred magnetically for 30 minutes. ZnS-Sm$^{3+}$ doped samples were prepared for three different concentrations of ZnS. The Sm$^{3+}$ concentration for all the samples were taken as 0.05M. The prepared samples were labeled as S1, S2, S3 and S4 where S1 contains only Sm$^{3+}$ in methanol whereas S2, S3 and S4 contain both Sm$^{3+}$ and ZnS in methanol with molar concentration of ZnS as 0.05, 0.15, 0.5 respectively.

The absorption spectra for the samples were recorded with a Shimadzu UV-2600 UV-Vis spectrophotometer by using methanol as reference. PL and excitation spectra were recorded with Horiba Jobin Yvon Fluoromax-4P spectrofluorometer. All the recordings were done at room temperature.

3. Result and Discussion

3.1. Absorption

Fig. 1 shows the absorption spectra in the UV-VIS region of the Sm$^{3+}$ co-doped with and without ZnS in Methanol. The Sm$^{3+}$ absorption peaks are observed at 287 nm ($^6$H$_{5/2}$→$^4$I, $^4$F$_{9/2}$), 345 nm ($^6$H$_{5/2}$→$^4$D$_{5/2}$), 363 nm ($^6$H$_{5/2}$→$^4$D$_{3/2}$), 376 nm ($^6$H$_{5/2}$→$^4$P$_{7/2}$), 390 nm ($^6$H$_{5/2}$→$^4$L$_{15/2}$), 403 nm ($^6$H$_{5/2}$→$^4$P$_{3/2}$), 417 nm ($^6$H$_{5/2}$→$^4$P$_{1/2}$), 440 nm ($^6$H$_{5/2}$→$^4$G$_{9/2}$), 464 nm ($^6$H$_{5/2}$→$^4$I$_{9/2}$), and 478 nm ($^6$H$_{5/2}$→$^4$I$_{11/2}$) [10-12,14]. Except the peak at 403 nm, all the peaks in the range 340-480 nm have very small intensity and expanded in the inset of Fig. 1. The 310 nm is the absorption peak of ZnS due to the electron-hole confinement in a small volume as a result of quantum size effect. The band-gap of the semiconductor is larger than the bulk semiconductor (335 nm) which confirms the particles are in the nano range [6]. The increase in intensity of the 310 nm absorption peak with the increase in concentration of ZnS, indicates the increase of particle number. The slight red shifting of this absorption peak might indicate the increase in particle size with the increase in ZnS concentration.

![Absorption Spectra](image)

Figure 1: Absorption spectra for singly doped Sm$^{3+}$ and ZnS co-doped Sm$^{3+}$ samples. Inset shows the expanded view of absorption spectra showing Sm$^{3+}$ transitions in the range 340-480 nm.
3.2. Excitation and Photoluminescence:

Fig. 2 shows the excitation spectra for S2, S4 and singly doped ZnS samples recorded in the range of 300-550 nm for emission wavelength fixed at 596 nm. For the Sm\(^{3+}\) doped samples, the spectra show maximum intensity for the excitation peak at 403 nm corresponding to \(^{6}\text{H}_{5/2} \rightarrow ^{6}\text{P}_{3/2}\) transition of Sm\(^{3+}\), because of the highest oscillator strength of the transition [2, 14, 15]. This fact is also revealed by the absorption spectra in Fig.1. The excitation spectrum of ZnS singly doped sample also shows a broad absorption in the range of 325 to 500 nm which considerably overlaps with the absorption maxima of samples S2 and S4. Another excitation spectrum for singly doped ZnS sample was recorded for the emission wavelength fixed at 550 nm (shown in Fig.3) which shows an excitation maxima at 403 nm. Based on the absorption and excitation studies, the excitation wavelength ($\lambda_{\text{exc}}$) was fixed at 403 nm for the PL recording of the samples. Moreover, due to the overlapping of the absorption spectra of S2 and S4 with that of singly doped ZnS sample, the absorption intensities for the ZnS co-doped Sm\(^{3+}\) samples enhance.

Fig. 4 reveals the PL spectra of the Sm\(^{3+}\) samples co-doped with and without ZnS. All the samples show four major PL peaks of Sm\(^{3+}\) at 560 nm ($^{4}\text{G}_{5/2} \rightarrow ^{4}\text{H}_{5/2}$), 596 nm ($^{4}\text{G}_{5/2} \rightarrow ^{4}\text{H}_{7/2}$), 642 nm ($^{4}\text{G}_{5/2} \rightarrow ^{4}\text{H}_{9/2}$) and 702 nm ($^{4}\text{G}_{5/2} \rightarrow ^{4}\text{H}_{11/2}$) [9, 13] respectively. It is observed that the intensities of all the PL peaks increase with the increase in ZnS concentration; the highest enhancement of the intensity being nearly one order of magnitude. The monotonous increase in the PL intensity with the ZnS concentration suggests that further enhancement of PL can be achieved with higher ZnS. Fig. 5 shows the PL spectra for singly doped ZnS sample whereas Fig. 6 shows the emission spectra of S4 in three different $\lambda_{\text{exc}}$ viz. 363 nm, 375 nm and 403 nm. For all the excitations (refer Fig. 6), though the PL peaks appear at the same positions, the intensity is highest for $\lambda_{\text{exc}}$ 403 nm due to its high oscillator strength. The PL intensities, Yields and FWHMs for all the observed PL maxima are shown in Table 1.

The mechanism leading to the enhancement of PL with the addition of ZnS is depicted by the energy level diagram shown in Fig. 7. The ZnS NPs possess different energy levels owing to the presence of defect states. The level $I_{\text{Zn}}$ originates due to Zn interstitials which is at an energy ~24814 cm\(^{-1}\) (~403 nm) above the valence band. The level $V_{\text{Zn}}$ arises due to Zn vacancy. When the sample is excited at 403 nm, two types of absorption take place. In the first mechanism, the Sm\(^{3+}\) ions absorb the excitation energy leading to the transition $^{4}\text{H}_{5/2} \rightarrow ^{4}\text{P}_{3/2}$. The excited electrons at $^{4}\text{P}_{3/2}$ then radiate non-radiatively and populate the $^{4}\text{G}_{5/2}$ level. In the second case, the ZnS NPs absorb the 403 nm excitation
Figure 4: PL spectra for S1, S2, S3 and S4 at 403nm excitation wavelength.

Figure 5: PL spectra of singly doped ZnS at 403nm excitation wavelength.

Figure 6: PL spectra of sample S4 for different excitation wavelengths.

Figure 7: Energy level diagram depicting the PL mechanism.

Table 1: PL intensities, Yield and FWHM for samples S1, S2, S3 and S4 under 403 nm excitations.

| PL maxima | PL Intensity | Yield | FWHM (nm) |
|-----------|--------------|-------|-----------|
|           | S1           | S2    | S3        | S4     |
| 560       | 8.39x10^5   | 1.4x10^6 | 2.68x10^6 | 2.72x10^6 |
| 596       | 2.17x10^6   | 5.72x10^6 | 6.91x10^6 | 8.39x10^6 |
| 642       | 2.24x10^6   | 5.15x10^6 | 6.71x10^6 | 8.76x10^6 |
| 560       | 1.32x10^7   | 2.32x10^7 | 6.30x10^7 | 5.78x10^7 |
| 596       | 4.05x10^7   | 9.77x10^7 | 1.66x10^8 | 1.66x10^8 |
| 642       | 3.877x10^7  | 9.47x10^7 | 1.74x10^8 | 1.98x10^8 |

|           | S1           | S2    | S3        | S4     |
| 560       | 13           | 13    | 30        | 19     |
| 596       | 17           | 15    | 20        | 16     |
| 617       | 15           | 15    | 26        | 17     |
and lift the valence band electrons to $I_{Zn}$. The electrons at $I_{Zn}$ recombine with the holes at $V_{Zn}$ thus emitting radiation at 550nm (refer Fig. 5) [16, 17]. This emitted energy is subsequently absorbed by the Sm$^{3+}$ ions in the ground state which further enhances the population of $^4G_5/2$. Radiative transition from the $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, $^6H_{11/2}$ respectively produces the PL maxima at 560nm, 596nm, 642nm and 702nm. The enhancement of PL intensity with concentration of ZnS can be attributed to the enhancement of the population of ZnS NPs around the Sm$^{3+}$ ions as well as the decrease in the distance between the ZnS NPs and Sm$^{3+}$ ions which enhances the efficiency of energy transfer from ZnS NPs to Sm$^{3+}$ ions.

4. Conclusion

In the present work, the absorption and PL behavior of Sm$^{3+}$ in presence of ZnS NPs in methanol medium has been studied. A monotonous enhancement in PL intensities and yield with the addition of ZnS NPs were observed for the studied samples. The enhancement is attributed to the effective increase of Sm$^{3+}$ absorption because of the addition of ZnS NPs. The study shows that the efficiency can be further enhanced with the increase in ZnS concentrations.

References

[1] Binnemans K. 2009 Chem. Rev. 109 4283.
[2] Jayasimhadri M., Cho E., Jang K., Lee H. and Kim S. 2008 J. Phys. D: Appl. Phys. 41 175101.
[3] Ricci P., Carbonaro C, Lehmann A., Congiu F., Puxeddu B., Cappelletti G.and Spadavecchia F. 2013 J Alloys Compd. 561 109.
[4] Jose G., C. Joseph, Ittyachen M. and Unnikrishnan N. 2006 Opt. Mater. 29 1495.
[5] Wageh S., Ahmed A., Ghamdi A. and Yakuphanoglu F. 2013 J. Sol-Gel Sci Technol. 66 443.
[6] Arago J., Lopez B., Cordoncillo E, Escribano P., Pelle F., Viana B. and C. Sanchez 2008 J. Mater. Chem. 18 5193.
[7] Sun L., Yan C., Liu C., Liao C., Li D. and Yu J. 1998 J. Alloys Compd. 275 234.
[8] Chen L., Zhang J., Lu S., Ren X and Wang X. 2005 Chem Phys Lett. 409 144.
[9] Tohda T., Fuji Y., Matsuoka T. and Abe A 1985 Appl. Phys. Lett. 48 95.
[10] Herrmann A., Kuhn S., Tiegel M., Russel C., Körner J., Klopfel D., Hein J. and Kaluza M. 2014 J. Mater.Chem.C 2 4328.
[11] Dillip G., Kumar P. and Raju B 2013 J. Lumin. 134 333.
[12] Deun R., Binnemans K., Warrand C. and Adam J. 1999 Proc. SPIE 3622, Rare-Earth-Doped Materials and Devices III, 175.
[13] Reddy C., Naresh V., Babu B. and S. Buddhudu 2014 Adv. Mater. Phys. Chem. 4 165.
[14] Suhasini T., Kumar J., Sasikala T., Jang K., Lee H., Jayasimhadri M., Jeong J., Yi S. and Moorthy L. 2009 Opt. Mater. 3 1167.
[15] Bokatial L. And Rai S 2012 J. Opt. 41 94.
[16] Taherian M., Alvani A., Shokrgozar M., Salimi R., Moosakhani S., Samee H., and Tabatabaeae F. 2014 Electron. Mater. Lett. 10 393.
[17] Wang X., Shi J., Feng Z., Li M. and Li C. Phys. Chem. Chem. Phys. 13 4715.