УДК 620.3

REVIEW: PHOTOLUMINESCENCE PROPERTIES OF UNDOPED AND Eu^{3+} DOPED ZnS NANOMATERIALS

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The PL properties of II-VI group semiconductor nanomaterials have been investigated depend of different synthesis method and other parameters. These group materials have interesting optical properties including PL properties of pure and doped materials. These group materials are mainly doped with rare earth metal for determine of improvement in the luminescence intensity. In this work we are analyzed PL properties of pure ZnS and Eu doped ZnS nanomaterials.

Keywords: luminescence properties, doped, zinc sulfide, nanomaterials.

1 INTRODUCTION

II-VI group semiconductor materials have great attention due to unique properties and great application fields. That's why researchers have been investigated different properties of such group's materials in detail. These group materials mainly have two different crystal structure –zincblende and wurtzite structures. Some of II-VI compounds have n-type conductivity, others have p-type conductivity and another set can have both types of conductivity (n-type and p-type). ZnO,CdS, CdSe and ZnS are of the n-type binary II VI compounds. One interesting properties of binary material is ZnS. The production of n-ZnS is more difficult than the others [1].

ZnS is known to be a direct band gap semiconductor and has immense interest among researchers because of its potential applications, such as optical coating, photoconductors, optical sensors, phosphors, window material, dielectric filter, the field emission display and also in LEDs [2, 3]. There are different synthesis method for to obtain nanosized ZnS compounds: Sol-Gel method, mechanochemical reaction method, chemical precipitation method, simple hydrothermal method, solid state reaction method, wet chemical method and etc. [4].

It is known that rare earth elements are effective luminescent centers [5–9]. Rare earth-doped luminescent II-VI materials, for example, Eu, Ce and Sm doped CaS and SrS, are promising candidates for application in color thin-film electroluminescence devices [6, 7]. The purpose of these studies is create a new type of luminescence material-doped semiconductor nanocrystal. ZnS is a good host because of its large band gap (E=3.6 eV). The application field of ZnS nanomaterials can be expanded by doped with rare earth elements and in here, rare earth element can be act luminescent centers. These researches are necessary for the expanding opportunity of the application field of this materials. There are many researches europium doped ZnS nanomaterials in literature. In these research, the PL properties were investigated depend on different synthesis method and other parameters. In this review, a different approach to the PL properties of europium doped zinc sulphide nanomaterials is applied.

2 PL PROPERTIES OF PURE ZNS AND EU^{3+} DOPED ZNS

2.1 Sputter deposition method

M. Aozasa and H. Chen were investigated ZnS:Eu electroluminescent devices with a single insulating layer were prepared by radio frequency magnetron sputtering[10]. In this experiment, they had been determined optimum concentration of europium dopant in the sputtering target. The dependence of the luminance of ZnS:Eu thin film electroluminescent devices on europium concentration in the sputtering target for the active layer. The maximum luminance L_{max} divided by the thickness d of the active layer is plotted to take the differences in the thickness into consideration. The thicknesses of the active layers of the samples subjected to the test are shown beside the plotted symbols. In the lower concentration region, the luminance increases with increasing europium concentration, reaching a maximum value at a europium concentration of about 0.94 mo1% and decreasing with further increase in europium concentration. A similar dependence was reported by Chase et al. [11]. The optimum europium concentration in the sputtering target is approximately 0.94mo1%. It is natural that the luminance decreases with decreasing europium concentration, because there could be no emission without luminescent centers. The decrease in the luminance at the higher concentration could result from the loss of electron energy necessary for the excitations due to the increased frequency of collisions between electrons and target molecules and concentration quenching [11].The concentration quenching could be due to resonant energy transfer, resulting in the loss of excitation energy by the cross-relaxation between the activators or the migration of the excitation. The formation of non-radiative centers or killers by the cohesion of the activators could be another cause of the concentration quenching. Although the luminance is not good enough for practical use, it is several times higher than that reported by Katayama et al. [12]. The saturation in the luminance is not observed; therefore, if a more stable insulating layer or double insulating layers are used, a higher luminance can be obtained. The emission peaks observed correspond well to the Eu^{3+} emission $^5D_0$-

^7D_s (J=0–3) [11], although the $^5D_0$-$^5D_3$ transition peak is a little bit too small. In order to obtain high luminance thin film electroluminescent devices, the dependence of the luminance characteristics on the substrate temperature for the deposition of the active layer was examined. The threshold voltage decreases when the active layer is prepared at elevated temperatures up to 450 °C. One of the reasons is the improvement in the crystallinity of the active layer, resulting in an increase in the electron mobility which easily causes an electron avalanche. The conduction current in the phosphor prepared at the higher temperature of 450 °C is larger than that in the phosphor prepared at the lower temperature and this result is consistent with the above-mentioned assumption that the carrier mobility can be improved by preparation at elevated temperatures.

2.2 Solvothermal method

Pure and europium (Eu)-doped zinc sulfide (ZnS) nanoparticles were synthesized by the solvothermal method by K. Ashwini, C. Pandurangapp and B.M. Nagabhushan [13]. PL studies of the samples were carried out at room temperature using a spectro-fluoremeter equipped with a 450 W xenon lamp as the excitation source. The PL spectra of Eu-doped ZnS nanocrystals were studied under 254 nm excitation. A strong emission was observed with its peak position centered at 390 nm. The PL intensity was found to increase with an increase in temperature from 300 to 500 °C. However, there is no significant change in the emission peak position. In Eu-doped ZnS the Eu ions are expected to be more stable in divalent (Eu^{2+}) state than in the trivalent (Eu^{3+}) state [14]. The researchers were observed in the present study is found to match well with the literature in the PL emission of Eu doped ZnS [15] and this indicates that Eu ions exist in the Eu^{2+} state. Also, the literature reveals that Eu-doped ZnO exhibits an emission at 400 nm due to Eu^{2+} ions and the emission peak is reported to be unaltered with an increase in temperature [16]. Therefore, the emission peak at 400 nm is found to be characteristic of Eu ions. Hence, there is no considerable shift in the emission peak position due to transition from the ZnS state to the ZnO state when heated to 500 °C. The emission centered at 390 nm in the present study may be attributed to Eu^{2+} ions [17]. It is observed that the peak intensities of the undoped samples are much smaller than those of the doped ones. This may be attributed to the effect of doping. When Eu ions are doped into ZnS nanoparticles, more defect states are introduced. This results in a reasonable increase in the peak intensities for the doped samples compared with the undoped ones. Also, in doped nanoparticles a large number of dopant centers are situated near the surface regions than in the interiors and hence are expected to give better emission efficiencies compared to pure ZnS. This is due to a high surface-to-volume ratio based on their small particle size. This is favorable for nucleation of the nanoparticles on the surface rather than interior of the samples. The high surface-to-volume ratio causes the surface states to act as luminescent quenching centers [18].

2.3 Solvothermal method

K. Ashwini, Yashaswini and C. Pandurangappa were prepared europium doped zinc sulfide nanocrystals (ZnS:Eu) by solvothermal method [19]. The PL studies of the samples are carried out at room temperature using spectrofluorimeter equipped with a 450 W Xenon lamp as the excitation source. The PL emission spectrum of Eu doped ZnS nanoparticles excited at 254 nm are shown. In 1 mol% Eu doped samples the PL emission spectrum is broad and symmetric with a prominent emission at 400 nm. However, with increase in concentration of Eu the PL emission spectrum becomes asymmetric and shows a series of side bands towards higher wavelength. The PL spectra show a prominent emission band peaked 400 nm besides three weak ones at 422, 485 and 530 nm. The emission at 422 nm is typical luminescence of ZnS resulting from the transition of electrons from shallow states near the conduction band to sulfur vacancies present near the valence band [20]. ZnS has a direct bandgap of 3.6 eV in which defect levels created by dopants form luminescence centers. On doping zinc sulfide with europium, the Eu^{2+} ions substitute the Zn^{2+} ions in the ZnS lattice and act as trap sites, where the electrons and holes can be trapped. An electron can undergo photo-excitation in the host ZnS lattice and subsequently decay to the defect level through a radiative transition. The strong emission at 400 nm could be attributed to the radiative decay between the localized states of Eu inside the ZnS band gap [21]. From the PL studies it is observed that the intensity of emission increases with increase in the dopant concentration. This may be attributed to the effect of doping. When Eu ions are doped into ZnS, more defect states are introduced. Also, in doped nanoparticles large number of dopant centers are situated near the surface regions than interiors and hence they give better emission efficiencies. This results in reasonable increase in the peak intensities with increase in the dopant concentration. Based on the literature the emission at 485 nm is attributed to the donor acceptor type defects centers [22]. The 530 nm green emission may be attributed to planar defects of the ZnS. They are due to the elemental sulfur species which are reported to be originated from the self-activated zinc vacancies of the ZnS nanostructures. It is proposed that for nanoparticles with reduced size, more zinc vacancies are located at the surface and they exhibit a dominant effect as green emission in the PL spectrum [23].

2.4 Sol–gel route in situ method

In this work, G. Earhart, B. Capoen and et all were reported ZnS semiconductor materials were prepared using the sol–gel route by an in situ method [24]. PL spectra of ZrO_2 thin films co-doped with ZnS and Eu^{3+} at different concentration ratios (ZnS:Eu = 10:2, 10:5 and 10:10). The results show clearly a decrease in the intensity of the ZnS nanoparticles PL band and an enhancement in the intensities of the Eu^{+3} bands with increasing Eu^{+3} concentration in the film. This observation means that the energy-transfer is more effective when the number of europium ions increases in the vicinity of the ZnS particles. This kind of measurement is used by several authors, as Kik and Polman [25], to emphasize the energy-transfer between the semiconductor nanoparticles and the rare-earth ions. Indeed, the enhancement factors measured for the 2, 5 and 10% Eu^{3+} co-doped samples in comparison with the 5% Eu^{3+} doped sample are 5, 10 and 13, respectively, which means that a competition occurs between the transfer and the quenching processes. In addition, the Eu^{3+} ions environment in the case of the co-doped system is slightly modified. This difference suggests a strong interaction between the matrix, the nanoparticles and the rare-earth ions, being able to modify the local symmetry of the ion. On its long-wavelength part, the emission spectrum of a 5% Eu^{3+}-doped film, together with the emission of a 15% ZnS–5% Eu^{3+} co-doped film, measured at 293 K and 10 K. These typical emissions of Eu^{3+} were obtained after decomposition of the spectrum in order to extract the contributions of emissions bands due to the semiconductor nanoparticles and those of the europium ion. More evidence of the energy-transfer is obtained with PLE spectra at 613 nm (Eu^{3+}: $^5D_0$ -$^7F_2$). On the sample doped with Eu^{3+} ions only, one can observe the absorption bands corresponding to the intra-4f transitions $^7F_0$ - $^5D_4$ (363 nm) and $^7F_0$ -$^5L_6$ (395 nm) [26]. For other samples, co-doped with ZnS and Eu^{3+}, the PLE spectra present broad bands beginning around 450 nm and level off below 355 nm. The difference between the PLE spectra with and without ZnS nanoparticles is the proof of the energy-transfer between semiconductor nanoparticles and rare-earth ions. Moreover, the fact that the PLE spectrum presents an efficient transfer for excitation wavelengths below 355 nm while the band gap of bulk ZnS corresponds to 336 nm (3.7 eV [27]), confirms that there exists a strong density of defect states. Thereby, in the case of this sample (15% ZnS–5% Eu^{3+}), the energy transfer involves intermediate defect states due to S^{2-} vacancies or Zn^{2+} interstitials. Indeed, measurements on this sample indicates that the real composition is 14.4% Zn–9.0% S–4.9% Eu, yielding the same ratio Zn: S equal to 1.6 as for the 20% ZnS-doped film.

2.5 Microwave-assisted solvothermal method

M. M. Ferrer, Cristiane W. R. and et. all were synthesis at different concentrations of europium- Eu^{3+} in zinc sulfide ZnS by microwave-assisted solvothermal method and investigated PL properties of all samples [28]. The PL emission spectra of pure and doped ZnS powders recorded at room temperature with excitation at 350.7 nm. The emission spectra show a broad band centered at ~484 nm which may be attributed to ZnS matrix, and the profile of emission band is typical of a multi-phonon and multilevel. A system in which relaxation occurs by several paths involving the participation of numerous states within the band gap of the semiconductor. The PL emission spectra of doped ZnS powders show that the maximum emission bands are centered at 498, 510, and 534 nm, for 1%, 2%, and 4% Eu^{3+}, respectively. Therefore, a red shift emission was observed with the increase of europium concentration. The emission spectra show the characteristic narrow band assigned to $^5D_0$-$^7F_2$ transitions in Eu^{3+} at 612 nm. The PL bands of three curves centered at 463.62 nm, 530.58, nm and 598.98 nm and their contributions in all doped samples. This suggests the incorporation of Eu^{3+} ion in the ZnS nanoparticles did not change its radiative relaxation processes. The red shift effect denotes a strong influence of the europium orange lines emission associated to the allowed transitions originated from electronic reconfiguration. To obtain a better understanding about the PL modifications in relation to the structural defects caused by the dopant, PL emission spectra were analyzed using decomposition. The contribution of each convoluted curve and its variations are depicted. Upon deconvolution, three pseudo-voids were chosen to describe the emissions; i.e., 463.62 nm (blue), 530.58 nm (yellow), and 598.98 nm (orange) labeled as a, b, and c, respectively. Pure ZnS has a greater contribution from the blue region; however, with the addition of europium and its increase, the contributions from the blue region decrease while the contribution from the orange region increases. The europium, besides its well defined bands, has modified the wide band of the matrix in the region between the orange and the red emissions, which indicates deep defects as a consequence of a different charge density in the lattice due to the Eu addition. To gain a better understanding of differences caused by the introduction of europium in PL results and the variations observed in the atomic orbitals, theoretical models of pure ZnS (p-ZnS) and doped ZnS (d-ZnS) were made. The doped models are not an exact replication of all modifications caused by the dopant in the lattice. The symmetry was maintained in both instances and the system d-ZnS has 3.125% of europium. Simulation results of band structure indicate a direct band gap at the Γ point in both models. The band gap values of p-ZnS and d-ZnS were 3.66 eVand 3.56 eV, respectively. Although there are limitations in simulating the experimental system, the theoretical and experimental results show the same behavior, i.e., the band gap decreases from pure to doped system. New localized states generated by the addition of Eu^{3+} in the forbidden band gap region increase the probability of fewer energy transitions which causes a red shift in the PL bands.

2.6 Coprecipitation reactions

ZnS:Eu nanocrystals were synthesized according to coprecipitation reactions [29]. In this work photoluminescent intensities of nanocrystal and ZnS:Eu synthesized using a new technique were 2.5 and 2.8 times higher than those of bulk phosphors. Similarly, the main PLE peak (monitored at 616 nm) of nanocrystal ZnS:Eu at 397 nm is due to $^7F_4$-$^5D_4$ transitions of Eu^{3+}.The excitation of nanocrystal ZnS:Eu is not related to charge-transfer state.

The dominant PL peak of nanocrystal ZnS:Eu excited by 397 nm light is observed at 616 nm due to $^5D_0$ - $^7F_2$ transitions of Eu^{3+}. The PL intensity of nanocrystal ZnS:Eu was 2.8 times higher than that of bulk ZnS:Eu,while the PLE peaks of the bulk remain unchanged with those of nanocrystal.

2.7 Noncoordinating solvent system

In this work David H. and Stephane P. were investigated the sensitization of luminescent lanthanide Eu^{3+} cations by the electronic structure of zinc sulfide (ZnS) semiconductor nanoparticles and samples were prepared by using a noncoordinating solvent system [30]. Excitation spectra collected while monitoring the lanthanide emission bands reveal that the ZnS nanoparticles act as an antenna for the sensitization of Eu^{3+}. In steady-state emission spectra for ZnS/Eu^{3+}, for λ_{ex} = 300 nm, a λ_{em} band was assigned at 460 nm (ZnS band); for λ_{ex} = 375 nm, a λ_{em} band was found at 455 nm (ZnS band); and for λ_{ex} = 440 nm, a λ_{em} band was found at 510 nm (ZnS band). These materials also display a red edge effect. The absence of broad emission with band maximum centered at 520 nm upon exciting the sample at 300 nm indicates that the samples under investigation in the present work do not have significant emission from Eu^{2+}. The excitation spectra of ZnS/Eu^{3+}, for λ_{em} = 410 nm (ZnS emission), λ_{ex} bands were identified at 255, 270, and 350 nm; for λ_{em} = 450 nm (ZnS emission), λ_{ex} bands were assigned at 260 and 370 nm; and for λ_{em} = 620 nm (attributed to Eu^{3+} emission), a λ_{ex} band appeared at 360 nm, with a broad excitation band centered at 510 nm (assigned to a charge transfer transition from anion valence band to Eu^{3+} ions; vide infra). The luminescence signal from the Eu^{3+} is not clearly evident in the steady-state spectra. However, it becomes prominent in time-gated mode (vide infra).

2.8 Chemical stirring method

ZnS nanoparticles doped with europium ions in a polymer matrix were doped during precipitation [31]. The PL spectrum consists of an onset at 330 nm, a shoulder at 315 nm, and a steep absorption edge at 280 nm. The corresponding band gap energy of 3.9 eV is larger than the one observed in bulk ZnS (3.7 eV). This can be explained as a quantum size effect, due to the electron-hole confinement in a small volume [32]. The particle size of ZnS was found to be around 4.0 nm, according to a calibration curve presented by Rossetti et al. [33]. By excitation at 395 nm, a pink-red photoluminescence peak appeared. The peaks can be attributed to the $^5D_0$ -$^7F_2$ (617 nm) and the $^5D_0$ -$^7F_1$ (586 nm) electronic transitions of $Eu^{3+,}$ which indicate that there are still some free Eu ions dispersed in the polymer matrix. Finally, nanoparticles' surface, resulting in Eu^{3+} activated ZnS. As expected, surface plays a significant role in the optical properties of such materials. The addition of Eu^{3+} to the outside of ZnS nanoparticles results in a totally different photophysical behavior, compared to the introduction directly inside the nanoparticles. The difference between ion-activated nanocluster and doped nanocluster has been studied thoroughly for Mn by the Sooklal et al. [34]. The photoluminescent spectra of doped and undoped ZnS nanocrystals in a polymer matrix. Upon excitation at 315 nm, the solutions were photoluminescent in the blue, with the emission peak positioned around 420 nm. Depending on the concentration of the europium ions present, the photoluminescence spectrum was blue-shifted as the concentration increased. The maximum luminescence was obtained when the dopant was about 2.5% molar percent. As we know, there are lots of surface defects working as energy traps in the nanoparticles, so that the photoluminescence of ZnS is frequently not observed at room temperature. In this work suggest that there are some Eu ions, dispersed on the surface of ZnS nanoparticles, working as modifiers to enhance the luminescence of ZnS nanoparticles. This could be interpreted as a passivation of sites of radiationless recombination.

2.9 Chemical stirring method

Eu^{2+} doped ZnS nanocrystals exhibit new luminescence properties were investigated by F.Q. Liu and Z.H. Hang [35]. The PLE spectrum recorded by scanning the excitation wavelengths while monitoring at 514 nm consists of two resolved absorption bands at 375 and 325 nm, respectively, which is red shifted from that of undoped ZnS. These two absorption bands should be due to the transition from energy levels in the midgap of ZnS host to excited states. The emission wavelength of 514 nm discussed here is not consistent to the red emission from 4 $f^6 5d^1$ - 4 f^7 transition in alkaline earth sulfide matrix. Because the 5d excited states of Eu^{2+} ion are host sensitive, i.e the $4f^6 5d^1$ states splitting due to spin-orbital coupling and crystal field may result in emission from blue to red [36]. To clarify the luminescence of Eu^{2+} ion in ZnS nanocrystals the measurements of dependence of PL, PLE and electron paramagnetic resonance on temperature are needed, which are now in progress.

2.10 Synthetic method

In this paper, synthesis of europium doped-zinc sulfide (Eu^{3+}:ZnS) spherical nanoparticles was carried out using freshly prepared zinc oxide (ZnO) nanorods precursor and synthetic method used was the precipitation technique [37]. The luminescence emission in the range 440 nm – 492 nm recorded for Eu^{3+}:ZnS nanoparticles can be ascribed to a self-activated centre formed between a Zn vacancy and a shallow donor associated with sulfur vacancy [38]. It is noted that the interstitially located Zn^{2+} were removed after conversion from ZnO to Eu^{3+}:ZnS. This is evident from the quenching of the violet band located at 413 nm. The removed interstitial Zn^{2+} might have been substituted by S^{2-} which has a larger ionic radius, thus increasing the strain in the ZnS host lattice. Interestingly, the intensity of the blue emission at 440 nm remains almost unaltered even after the conversion of ZnO into Eu^{3+}:ZnS, confirming our earlier argument that the blue emission was due to Zn vacancies. The blue-yellow emission band at 520 nm could be formed by the transfer of trapped electrons on the sulfur vacancies to interstitial sulfur states [39]. In addition to the defects related emission bands of ZnS host, transition bands such as $^5D_0$-$^7F_1$ (590 nm – 592 nm), $^5D_0$-$^7F_2$ (614 nm – 629 nm), $^5D_0$-$^7F_5$(758 nm) and $^5D_0$-$^7F_6$ (882 nm) which are related to Eu^{3+} can also be observed under resonant excitation. No such transitions were observed for Eu^{3+}:ZnS spherical nanoparticles under nonresonant excitation at 285 nm demonstrating that no energy transfer from the host ZnS to Eu^{3+} ions using this synthetic procedure, rather transition bands such $^5D_0$-$^7F_5$ and $^5D_0$-$^7F_6$ which are seldom observed were recorded for this sample.

2.11 Atomic layer epitaxy method

Zinc sulphide thin films doped with europium have been grown by the atomic layer epitaxy method [40]. In this work were observed the red emission from the 5D, level of Eu^{3+} could be detected and the emission could be excited via the band gap of ZnS indicating that hydrogen sulphide does not reduce europium when reacting with Eu^{3+}, but that europium remains trivalent.

2.12 Modified precipitation method

In this work luminescent properties of Eu^{3+}doped zinc sulfide nanocrystal were investigated [41]. Eu^{3+} doped zinc sulfide nanocrystals were prepared by a modified precipitation method. The Eu^{3+} ion has $4f^6$ electron configuration and the spectra are observed on the excitation spectra of the $^5D_0$–$^7F_1$ transition of these ions. Normally, Eu^{3+} generates luminescence due to the transition from the excited $^5D_0$ level to the ^7F levels of the $4f^6$ configuration. The transition in $^5D_0$–$^7F_1$ (about 593 nm) results from magnetic coupling. Because of crystal-field transition, $^7F_1$ is split to produce blue emission. In order to interpret the excitation spectra of ZnS:Eu nanocrystal, one has to consider that Eu^{3+} ions can be excited to 4f higher energy state, and also to the transition state of electric charge because Eu^{3+} becomes the complex ions with sulfur ions in the crystal grating of ZnS. Transition state of electric charge is that an electron is transited to one ion from another ion, that is the electron in 3p-electron state of sulfur ion is transited to 4f-electron state of Eu^{3+} ion, so the Eu^{3+} is turned into Eu^{2+} and the S^{2-} is turned into S^-. This is not a normal excitation process, because the luminescence is not a contrary process of excitation. When the electron is returned to surrounding ions from the state of the charge transition, the excitation energy are passed to Eu^{3+} ions, and so Eu^{3+} ions with the excitation energy may transit to ^5D state, and produce luminescence. This excitation is called to the excitation of the charge transition, and the excitation is line spectra, and the excitation between the 4f states of Eu^{3+} ions is band spectra. In ZnS host lattice, when Zn^{2+} ion is replaced to $Eu^{3+,}$ the surrounding of Eu^{3+} has produced some defects because of the difference in the valence state. Because of different defects, the sites of Eu^{3+} in the crystal lattice are also different. The excitation and emission spectra of ZnS:Eu colloid with the surfactant are investigated. There are four emission spectra, such as 452.8, 592.0, 617.2 and 695.4 nm. The band at 452.8 nm results from water solution. The emission lines at 592.0, 617.2 and 695.4 nm result from the transition of $^5D_0$–$^7F_1$, $^5D_0$–$^7F_2$ and $^5D_0$–$^7F_3$, respectively. The reasons of the transitions may be that the different symmetry of Eu^{3+} ions in some areas produced different emission sites because of the charge compensation. The Eu^{3+} ions are substituted for Zn^{2+} ion in the host lattice, so charge compensation exists. For keeping the system neutral, the residual charges of Eu^{3+} ions are compensated by some defects, such as the compensation of S^{2-} ions in a crack: the O^{2-} ions are replaced S^{2-} ions into the crystal grating to compensate. The surrounding of Eu^{3+} ions may be different because of different compensating forms, so different sites of emission are generated, and so on. The other results from the charge transition between Eu^{3+} and O^{2-} because the ZnS host materials has no absorption bands. From the results are observed the strength of the emission band is different with different amount of doping Eu^{3+} ions. The strength of the emission is directly proportional to the amount of doping Eu^{3+} ions.

CONCLUSION

In the Eu^{3+} doped ZnS, there are three emission sites of ZnS:Eu nanocrystals from the transitions of $^5D_0$–$^7F_1$, $^5D_0$–$^7F_2$ and $^5D_0$–$^7F_3$, respectively. The PL emission spectra showed an increase in PL intensity due to heating in undoped ZnS nanocrystals. At the same time the doping of Eu enhanced the emission efficiency of nanocrystalline ZnS. The PL studies of Eu doped ZnS nanoparticles reveal that for low concentration of Eu the PL emission spectrum is broad and symmetric with a prominent emission at 400 nm. However, with increase in Eu concentration the PL emission spectrum becomes asymmetric and shows a series of side bands towards higher wavelengths. The PL spectra show that Eu ions act as trap sites in the ZnS lattice. With increase in concentration of Eu the intensity of PL emission increases due to increase in defect sites and traps. So, ZnS:Eu nanocrystal-polymer composites exhibit enhanced luminescence and excellent thin film processibility, a further step is to try their capacity as electroluminescent devices.

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ШОЛУ: ЛЕГИРЛЕНБЕГЕН ЖӘНЕ Eu^{3+}-ПЕН ЛЕГИРЛЕНГЕН ZnS НАНОМАТЕРИАЛДАРЫНЫҢ ФОТОЛЮМИНЕСЦЕНТТІК ҚАСИЕТТЕРІ

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Синтездің әртүрлі әдістеріне және басқа да параметрлерге байланысты II-IV топтағы жартылай өткізгіш наноматериалдардың фотолюминесценттік қасиеттері зерттелді. Бұл топтардың материалдары қызықты оптикалық қасиеттерге ие, соның ішінде таза және легирленген материалдардың фотолюминесценциясына ие. Аталған топтардың материалдары люминесценцияның қарқындылығын жақсарту үшін негізінен сирек кездесетін металлмен легирленеді. Осы жұмыстың барысында Eu қоспаланған таза ZnS және ZnS наноматериалдарының фотолюминесценттік қасиеттеріне талдау жасалады.

Кілт сөздер: люминесценттік қасиеттер, легирлеу, мырыш сульфиді, наноматериалдар.

ОБЗОР: ФОТОЛЮМИНЕСЦЕНТНЫЕ СВОЙСТВА НЕЛЕГИРОВАННЫХ И ЛЕГИРОВАННЫХ Eu^{3+} НАНОМАТЕРИАЛОВ ZnS

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Исследованы фотолюминесцентные свойства полупроводниковых наноматериалов II-IV групп в зависимости от различных методов синтеза и прочих параметров. Материалы этих групп обладают интересными оптическими свойствами, в том числе фотолюминесценцией чистых и легированных материалов. Материалы этих групп в основном легируются редкоземельным металлом для улучшения интенсивности люминесценции. В ходе развития данной работы, анализируются фотолюминесцентные свойства наноматериалов из чистого ZnS и ZnS, легированного Eu.

Ключевые слова: люминесцентные свойства, легирование, сульфид цинка, наноматериалы.