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Study of the optical properties of Eu^{3+}-doped ZnS nanocrystals

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Abstract

Absorption and photoluminescence excitation spectra are presented for ZnS:Eu nanocrystals. The average size of the ZnS:Eu nanocrystals was about 3.6 nm deduced from the absorption spectra and was independent of the doping concentration of Eu^{3+}. The characteristic luminescence from the $^5D_0$–^7F_J (J=0, 1, 2) transition of Eu^{3+} was observed. This is attributed to the electrons and holes being localized around Eu^{3+}, and the possibility of energy transfer from band to band excitation in ZnS to trivalent rare earth Eu^{3+} is increased. The location of Eu^{3+} is different for different doping concentrations deduced from the relative luminescence intensity. Three main types of Eu^{3+} ion exist in the colloid. The samples undergo growth and aging processes according to the variation of the luminescence intensity after preparation. A tentative explanation is given that the location of the Eu^{3+} ions and the surface states may play important roles. © 1998 Elsevier Science S.A.

Keywords: Colloid; Growth and aging processes; Surface states; ZnS nanocrystals

1. Introduction

A new kind of luminescence material-doped semiconductor nanocrystal has been the focus of recent research [1,2]. ZnS is a good host because of its large band gap (E_g~3.6 eV). It has been used commercially as a phosphor and a thin film electroluminescent device, especially if doped with transition metals or rare earth ions acting as luminescent centers [3]. ZnS nanocrystals doped with optically active luminescent centers create new opportunities in luminescence studies regarding the application of nanocrystals [4]. Research on this kind of nanocrystal is necessary to understand the correlation between the host nanocrystals and the doped luminescent centers. We reported earlier the characteristic optical properties of ZnS:Mn nanocrystals [5]. By measuring spectra at different times, we can distinguish two processes – the growth and aging processes – according to the change in the luminescence intensity and the position of the absorption peaks.

Here we report the preparation and the characteristic optical properties of Eu^{3+}-doped ZnS semiconductor nanocrystals in alcohol colloid systems.

2. Experiment

The samples were prepared by the colloid method. Alcohol solutions of zinc acetate ($Zn(CH_2COO)_2$), methacrylic acid ($C_5H_8O_2$) and europium chloride ($EuCl_3$) were freshly prepared. The zinc acetate solution was placed in a reaction vessel and mixed with methacrylic acid with continuous stirring. H_2S gas was introduced into the mixed solution. $EuCl_3$ solution was then added dropwise into the mixture. The rate of addition was controlled by a fixed-flow console pump (Gilson, M312) at a rate of 1.0 ml min^{-1}. The prepared ZnS:Eu^{3+} alcohol colloidal solution was quite transparent and suitable for optical experiments.

The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of Eu^{3+} in ZnS nanocrystals were recorded with an Hitachi F-4000 fluorescence spectrometer. The excitation light source was a 150 W Xe lamp, and the emitted light was detected by a R928 photoamplifier tube (PMT) with a resolution of 1.0 nm. The recorded

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spectra were corrected automatically for PMT response. UV absorption spectra were recorded by a Shimadzu UV-1206 spectrophotometer. All syntheses and experiments were performed at room temperature.

3. Results and discussion

The radius of ZnS nanocrystals can be deduced from the absorption edge of the UV absorption spectra [6]. If the radius of the nanocrystal is comparable to the excitonic Bohr radius (~5.0 nm for ZnS), its electronic properties will change. The energy band for the bulk splits into discrete energy levels for the nanocrystals. Moreover, the band gap increases and the edge of the absorption spectrum shifts towards the blue, which demonstrates the quantum size effect. For our samples, the absorption edge shifts toward the red with an increase in the Zn^{2+} concentration, and it will also change a little for different S^{2-} concentrations, temperature, etc. [7].

The absorption spectrum of a ZnS:Eu nanocrystal is shown in Fig. 1; the concentration of Zn^{2+} is 1.0×10^{-3} mol l^{-1}. The band edge is located at about 290 nm and the particle size is almost 3.6 nm [1]. The Eu^{3+} concentration is different for the three samples used in our experiment. For samples 1, 2 and 3, the Eu^{3+} doping concentration is 1.0×10^{-5}, 2.0×10^{-5} and 5.0×10^{-5} mol l^{-1}, respectively. They have the same size since their absorption edges have similar positions. As reported previously [2], addition of the dopant cannot change the average size of the nanocrystals, but it can increase the size distribution significantly, as indicated by the absorption spectra – the absorption peak appears as a shoulder.

For most semiconductor nanocrystals, two kinds of emission bands can be observed, which are related to the excitonic luminescence and the impurity or defect luminescence. The former is sharp and is located at the absorption edge, the latter is broad and shifts towards the red compared with the absorption edge. For ZnS nanocrystals, only one emission band is detected, which is attributed to a sulfur vacancy or interstitial sulfur lattice defects [8]. For Eu^{3+}-doped ZnS nanocrystals, besides the ZnS emission band, the characteristic emission from the doped Eu^{3+} ions was also observed. For the ZnS:Eu bulk sample, three emission peaks can be detected which correspond to the $^5D_0$–^7F_J ($J=0,1,2$) transition from Eu^{3+}. Fig. 2 shows the PL spectra of the three samples excited at 290 nm. The position of the luminescence peaks does not shift much with that of the bulk, but the relative intensity of the peaks is different for the three samples. Details of the emission peaks and their assignment are listed in Table 1. From the relative intensity of the peaks, the symmetry of Eu^{3+} in the ZnS host can be deduced.

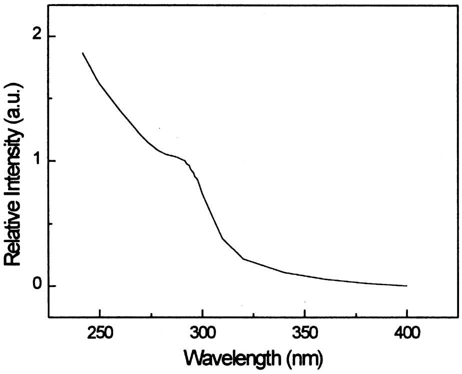

Fig. 1. Absorption spectra for ZnS:Eu nanocrystals.

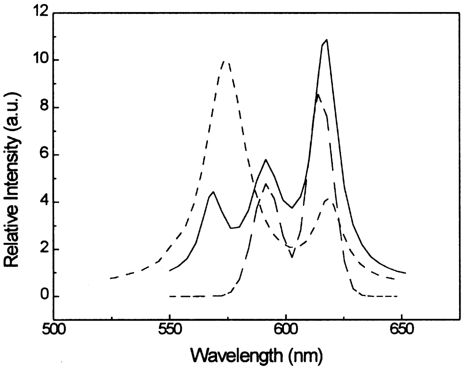

Fig. 2. Photoluminescence spectrum for ZnS:Eu nanocrystals; ex.: 290 nm (Eu^{3+} concentration: (· · ·) 5.0×10^{-5}, (———) 2.0×10^{-5} and (- - -) 1.0×10^{-5} mol l^{-1}).

It is well known that the $^5D_0$–$^7F_2$ transition is an electric dipole transition in nature and the $^5D_0$–$^7F_1$ transition is a magnetic dipole transition. If Eu^{3+} occupies the sites with an inversion center, the $^5D_0$–$^7F_2$ electric dipole transition is forbidden and its luminescence intensity should be weak, while the $^5D_0$–$^7F_1$ transition is permitted and the luminescence intensity should be relatively strong. If Eu^{3+} occupies the sites without an inversion center, the $^5D_0$–$^7F_2$ electric dipole transition will be permitted and the luminescence intensity will be much stronger than that of the $^5D_0$–$^7F_1$ transition. From this analysis, we expect that Eu^{3+} ions occupy sites with different symmetry for different doping concentrations. The probable reason for this is that a proportion of the Eu^{3+} ions cannot enter the lattice and substitute for Zn^{2+}.

For this kind of ZnS:Eu nanocrystal, the position of Eu^{3+} can be classified into three types: (1) Eu^{3+} can be at the zenith of the ZnS lattice co-occupied by the multi-ZnS nanocrystal because of the size and valence of Eu^{3+}; (2)

Table 1
The luminescence peak positions and the assignment of the three samples

Sample	Luminescence peaks (nm)	Origin of the peaks
1	593, 617	$^5D_0$–$^7F_1$, $^5D_0$–$^7F_2$
2	574, 593, 617	$^5D_0$–$^7F_0$, $^5D_0$–$^7F_1$, $^5D_0$–$^7F_2$
3	574, 619	$^5D_0$–$^7F_0$, $^5D_0$–$^7F_2$

Eu^{3+} are surrounded by ZnS nanocrystals; and (3) most of the Eu^{3+} ions are adsorbed physically on the surface of the ZnS nanocrystals. The probability of the three types depends not only on the Eu^{3+} concentration during processing, but also on the micro-crystal field around Eu^{3+}. These factors make the location of Eu^{3+} complicated and this is responsible for the abnormal behavior observed in Fig. 2. The linewidth of Eu^{3+} emission is broadened compared with that of the bulk. Two reasons can be forwarded to explain this phenomenon: (1) the size distribution of the ZnS nanocrystals is large; (2) the crystallinity of ZnS is not complete in the colloid [2].

The PLE spectrum can be obtained by monitoring the 617 nm luminescence peak and, as shown in Fig. 3, it has the same shape and peak position as that of undoped ZnS nanocrystals. This is also a demonstration that Eu^{3+} emission comes from the excitation of the ZnS host. The possible route to accomplish this kind of energy transfer is that the electrons and holes are confined to be near Eu^{3+} in such small nanosize ZnS particles and the energy transfer probability from the ZnS host to Eu^{3+} is increased. This mechanism is the same as reported for ZnS:Mn colloids [8]. Compared with the absorption edge, the excitation peak shifts towards the red. A possible reason for this is the larger the particles, the greater the contribution to the luminescence intensity.

The absorption spectra are unchanged after preparation but the luminescence intensity changes drastically. As an example, the change of the 574 nm peak intensity with time for sample 2 is shown in Fig. 4. The intensity reaches its maximum after 14 h, and then decreases rapidly until, after 50 h, it is difficult to detect. This behavior is similar to that observed for ZnS:Mn colloids [1,8]; we called them growth and aging processes with respect to the increasing and decreasing intensity periods. Two responsible reasons are considered for the increase in the luminescence intensity. One is the increased number of Eu^{3+} ions that participate in the radiative transition, although they are surrounded or co-occupied by ZnS nanocrystals, and adsorbed on the surface of the ZnS host. The other is surface passivation by the surfactant, and this can reduce the number of dangling bonds on the particle surface; the nonradiative relaxation path for electrons excited into the conduction band can be effectively blocked. These two processes compete with each other during the growth period. As for which is dominant, detailed research should be conducted.

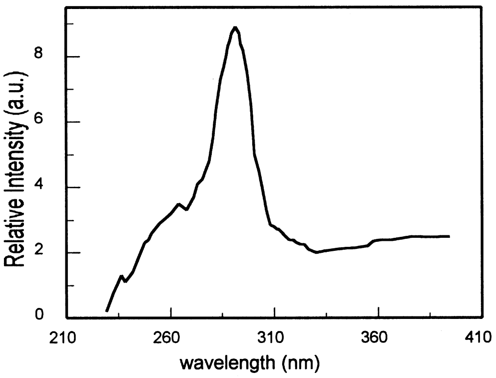

Fig. 3. Excitation spectra for ZnS:Eu colloids; em.: 617 nm.

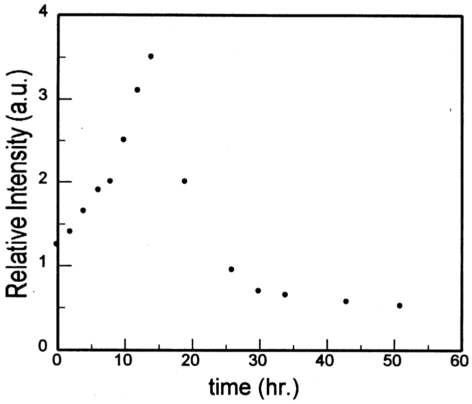

Fig. 4. The luminescence intensity changes with increasing time after preparation.

After reaching its maximum, the intensity decreased with time. A possible reason for this is that the surface modification deteriorates and the nonradiative relaxation path is increased [2]. A schematic energy-level model of the ZnS nanocrystal, the doped Eu^{3+} ion and the surface states are shown in Fig. 5. Surface passivation is realized by the electrons filling the empty surface states. These filled surface states are metastable. As the keeping time increases, the electrons in the surface states will decay to lower energy levels [5]. This makes the nonradiative path increase and the luminescence intensity decrease.

For ZnS:Eu nanocrystals, the above processes only last for a short period. A tentative explanation is that most of the Eu^{3+} ions are only adsorbed on the surface of ZnS nanocrystals and they cannot substitute the Zn^{2+} sites in the ZnS lattice. This is reasonable because the larger radius

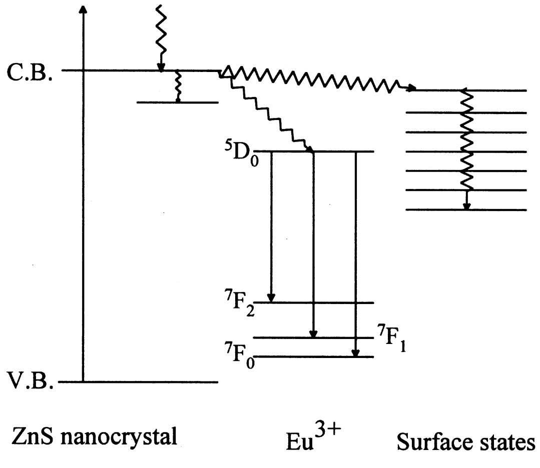

Fig. 5. Schematic energy-level model of the ZnS nanocrystal, the doped Eu^{3+} ion and the surface states.

of Eu^{3+} (0.95 Å) compared with Zn^{2+} (0.74 Å) makes it difficult for Eu^{3+} to enter the lattice. Other evidence is that the deteriorated surface states can be recovered by irradiation with UV light from a Xe lamp and the PL intensity increases during the processing [9]; this is called IILE (irradiation induced luminescence enhancement). For the aged ZnS:Eu samples, the luminescence intensity recovered on exposure to UV light, but it cannot reach the maximum value obtained during the growth process. This can be interpreted as the desorption of Eu^{3+} from the surface of ZnS and desorbed Eu^{3+} do not contribute to the IILE.

In summary, the optical properties of ZnS:Eu nanocrystals in alcohol colloidal systems are reported. The doping concentration has no effect on the size of the nanocrystals, but the size distribution is broadened. The complexity of the location of Eu^{3+} is deduced from the PL spectra. A proportion of the Eu^{3+} ions is co-occupied or surrounded by ZnS nanocrystals, the remainder is only adsorbed on the surface of the ZnS nanocrystals. The luminescence intensity increases to its maximum and then decreases with time after preparation. From the consistency of this effect with that occurring for ZnS:Mn nanocrystals in a colloid system, we can divide this process into growth and aging processes. These processes are completed in about 50 h and they are short compared with that of ZnS:Mn colloids. The relative position of Eu^{3+} and the ZnS nanocrystals is different from Mn^{2+} in the ZnS lattice. This difference can also be confirmed by IILE with UV light from a Xe lamp.

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