

Energy structure and fluorescence of Eu^{2+} in ZnS:Eu nanoparticles

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Eu^{2+} -doped ZnS nanoparticles with an average size of around 3 nm were prepared, and an emission band around 530 nm was observed. By heating in air at 150 °C, this emission decreased, while the typical sharp line emission of Eu^{3+} increased. This suggests that the emission around 530 nm is from intraion transition of Eu^{2+} . In bulk ZnS:Eu^{2+} , no intraion transition of Eu^{2+} was observed because the excited states of Eu^{2+} are degenerate with the continuum of the ZnS conduction band. We show that the band gap in ZnS:Eu^{2+} nanoparticles opens up due to quantum confinement, such that the conduction band of ZnS is higher than the first excited state of Eu^{2+} , thus enabling the intraion transition of Eu^{2+} to occur.

Doped semiconductor nanoparticles are interesting nanostructured materials because their electronic and optical properties, which are largely size dependent, may result in practical applications such as high brightness displays. A typical such material is ZnS:Mn nanoparticles which have been widely studied.¹ Recently, the luminescence properties of trivalent rare-earth (RE) ions [Tb^{3+} (Ref. 1), Eu^{3+} (Ref. 2)] in semiconductor nanoparticles have been reported. The luminescence of Eu^{2+} and Eu^{3+} in xerogels^{3,4} was also examined. However, to our knowledge, divalent RE ions doped into semiconductor nanoparticles have received little attention.

Eu^{2+} -doped ZnS is a promising phosphor. The advantage of this phosphor over other Eu^{2+} -doped sulphides (CaS, SrS, and BaS) is that ZnS is more chemically stable. However, it was reported that instead of luminescence from Eu^{2+} , only the Eu^{2+} -bound exciton could be observed in bulk ZnS:Eu^{2+} , because the excited states of Eu^{2+} are higher or degenerate within the host conduction band.^{5,6} In this paper, we show that as the size of ZnS:Eu particles approaches a critical dimension, emission from Eu^{2+} becomes possible, and we argue that this is due to the fact that the energy structure of ZnS:Eu^{2+} is modified by quantum size confinement.

ZnS:Eu^{2+} nanoparticles were prepared as follows: A four-neck flask was charged with a solution containing 10-ml methacrylic acid, 5-g citric acid, and 1000-ml ethanol (99.95%). The solution was stirred under N_2 for 2.5 h. A second solution containing 8.009 g of Na_2S and 200 ml of ethanol, and a third solution containing 30.337 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$, 0.114 g of EuCl_2 and 200 ml of ethanol ($\text{Eu}^{2+}/\text{Zn}^{2+}$ molar ratio 5:995) were prepared and added to the first solution simultaneously via two different necks. After the addition, the resulting solution was stirred constantly under N_2 at 80 °C for 24 h. The pH value of the final solution was 2.4. This relatively low pH value is required to prevent the precipitation of unwanted Eu species from occurring. The nanoparticles were extracted from the solution by centrifugation, and dried in vacuum at room temperature.

The nanocrystalline structure, size, and shape were observed by x-ray powder diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). The XRD pattern was recorded with an INEL diffractometer using a CPS 120 detector and a monochromatized $\text{Cu K}\alpha 1$ ($\lambda = 1.54056 \text{ \AA}$) radiation with $\alpha\text{-Si}$ ($a = 0.543 \text{ nm}$) as an internal standard. The particles were suspended in ethanol, and brought onto a holey carbon covered copper grid for

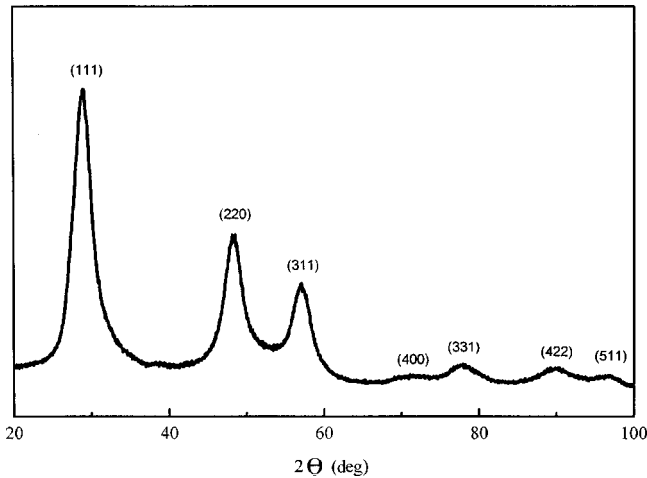


FIG. 1. X-ray-diffraction pattern of ZnS:Eu²⁺ nanoparticles.

HRTEM observation. The HRTEM images of the particles were obtained using a JEM-4000EX electron microscope (400 kV) with a structural resolution of 0.16 nm.

The absorption spectra of the particles were measured in a JASCO V-530 UV/visible spectrophotometer. The photoluminescence excitation and photoluminescence were recorded at room temperature using a SPEX 510 fluorescence spectrophotometer. All measurements were carried out at room temperature.

XRD measurement shows that the ZnS:Eu particles are characteristic of that of the zinc-blende modification of ZnS (sphalerite, Fig. 1). The average size of the particles, calculated from the Debye-Scherrer equation, is around 3 nm. A typical HRTEM image (Fig. 2) shows that the average size of the particles is about 3 nm, in agreement with the XRD and optical-absorption measurements. The (111) lattice planes of some particles can be observed in the HRTEM images. The (111) lattice spacing of the particles was estimated to be around 0.31 nm from the HRTEM images. This is consistent with the (111) spacing of bulk ZnS (0.312 nm).

A broad emission at 530 nm was observed from the ZnS:Eu nanoparticles (Fig. 3). In order to reveal whether this emission is from Eu²⁺, we oxidized the sample by heating it in the air at 150 °C for 1 and 12 h, respectively. Since Eu²⁺ is not stable in an oxidized atmosphere, it can be oxidized to Eu³⁺ easily via $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+} + e$. The electron may be

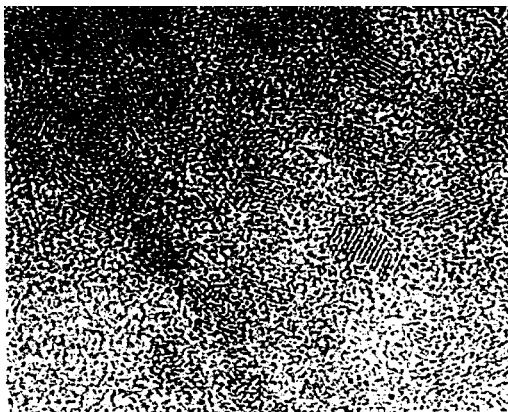


FIG. 2. High-resolution transmission electron microscopy (HRTEM) image of ZnS:Eu²⁺ nanoparticles.

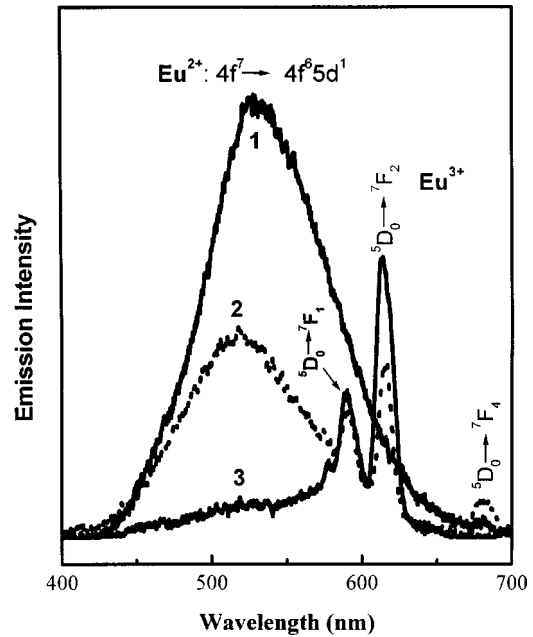


FIG. 3. Emission spectra of ZnS:Eu nanoparticles as prepared (1) and after heating at 150 °C for 1 (2) and 12 h (3), respectively (excitation at 260 nm).

trapped at the surface states or defects of the particles. After oxidation, the intensity of the broad emission at 530 nm decreased, while a new sharp band appeared around 612 nm and grew gradually as increase in oxidation time. After oxidation for 12 h, the broadband at 530 nm, almost disappeared, while three sharp bands around 590, 612, and 695 nm were observed (Fig. 3). These three bands are the characteristic emissions of Eu³⁺,⁷ corresponding to the transitions of ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$, and ${}^5D_0 \rightarrow {}^7F_4$, respectively. These results demonstrate that the emission at 530 nm is indeed from Eu²⁺. After oxidation, the concentration of the Eu²⁺ ions decreases, while the concentration of Eu³⁺ increases, resulting in a decrease in the emission intensity of Eu²⁺ at 530 nm and in an increase of the emission intensity of Eu³⁺ ions. There is no ZnSO₄ or ZnO reflections detected in XRD measurements in the oxidized samples, indicating that upon oxidation at such low temperatures, the conversion of ZnS to ZnSO₄ or ZnO is negligible.

Figure 4 shows the optical absorption (ABS), photoluminescence excitation spectra of ZnS:Eu²⁺ nanoparticles as prepared and the absorption spectrum of bulk ZnS. The exciton absorption at ~290 nm is blueshifted by ~45 nm from the bulk value [~335 nm (Refs. 8 and 9)] because of quantum size confinement. Using the exciton absorption energy and based on the tight-binding model,¹⁰ the estimated particle size is around 3 nm. This is in agreement with XRD and TEM observations. Three absorption bands appear in the photoluminescence excitation spectrum (Fig. 4). One absorption band is on the longer-wavelength side of the particle absorption edge. It is probably from the absorption of the doped Eu²⁺ ions. The excitation signals from these states indicate that there is an emitting state within the band gap, and that the energy scheme in nanophase ZnS:Eu²⁺ is different from that of bulk ZnS:Eu²⁺. Due to quantum confinement, the energy gap of ZnS is increased to approach the level of SrS (for example, the energy gap is ~4.5 eV for a

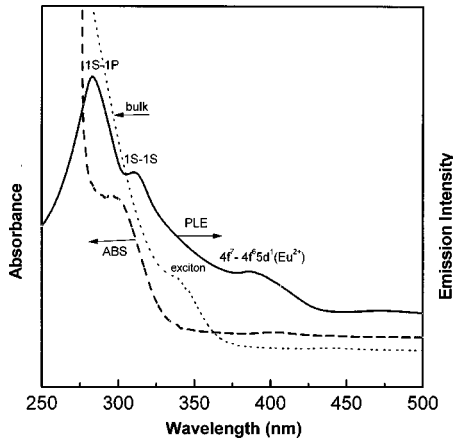


FIG. 4. Optical absorption (ABS) and photoluminescence excitation (PLE, emission of 530 nm) spectra of ZnS:Eu^{2+} nanoparticles and absorption spectrum of bulk ZnS .

3-nm-sized ZnS particle, and is 4.3 eV for SrS (Ref. 11)). Thus the energy schemes of Eu^{2+} in ZnS and in SrS might be similar, and may have analogous luminescence properties. For example, the excitation or emission spectrum of Eu^{2+} in ZnS nanoparticles is very similar to the excitation or emission spectra of Eu^{2+} in SrS:Eu .¹¹ By comparing the excitation spectrum of ZnS:Eu^{2+} nanoparticles (Fig. 4) with that of SrS:Eu^{2+} ,¹¹ and according to the calculation based on effective-mass approximation,⁹ we assign the two excitation bands at 280 and 310 nm to the $1S-1P$ and $1S-1S$ transitions of ZnS ,¹²⁻¹⁴ respectively. The band in the range of 380–430 nm corresponds to the $4f^7 \rightarrow 4f^6 5d^1$ transitions of Eu^{2+} ions.

The emission spectra of the particles excited at 260, 340, and 390 nm are shown in Fig. 5. The emission at ~ 530 nm is from the $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions rather than from the so called Eu^{2+} bound exciton, because the emission wavelength is shorter than that of the bound exciton. In addition, the bound exciton is not stable at temperatures above

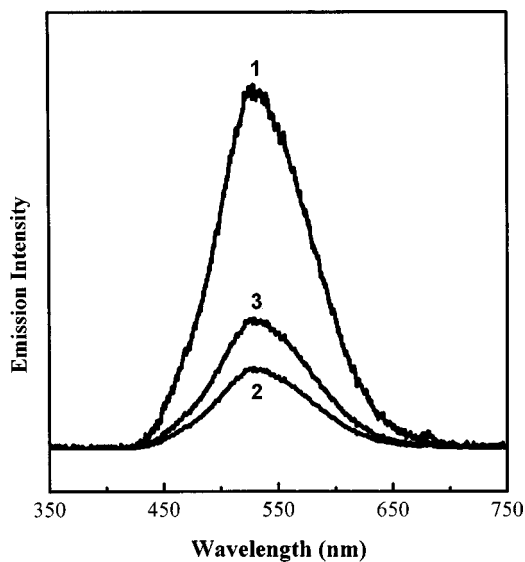


FIG. 5. Emission spectra of ZnS:Eu^{2+} nanoparticles obtained by excitation at 260 (1), 340 (2), and 390 (3) nm, respectively.

200 K.¹⁵ We can see that the emission wavelength is the same for excitation at 260, 340, or 390 nm, but the emission intensity obtained by excitation at 260 nm is higher than that obtained at 340 or 390 nm. In doped semiconductors, there are two channels of excitations in the impurity luminescence. One is indirect excitation, i.e., excitation into the conduction band of the host, followed by an energy transfer from the host to the impurity ions to cause the luminescence. The other is direct excitation of the impurity ions. The absorption edge of the particle is around 290 nm. Thus the excitation at 260 nm is an indirect excitation, while excitation at 340 or 390 nm is a direct excitation. It is clear that the luminescence obtained by indirect excitation of the host is much more efficient than that obtained by direct excitation of Eu^{2+} itself, since for below-gap excitation only little of the exciting light is being absorbed.

In bulk ZnS:Eu^{2+} , the ground state of Eu^{2+} is 2.25 eV below the edge of the conduction band, and its first excited state is ~ 0.35 eV above the edge of the conduction band in bulk ZnS .⁵ The excited states of Eu^{2+} are degenerate with the continuum of the conduction band. Photoionization easily occurs, and no intraion transition was observed because the intraion excitation process requires a higher energy than that for the photoionization transition. Emission from this state is possible only if there is a potential barrier for the autoionization of the center. However, such a barrier does not exist in the case of Eu^{2+} in bulk ZnS , and thereby no intraion transition was observed.¹⁵ The emission bands of bulk ZnS:Eu around 700 nm (Ref. 15) are attributed to the so-called anomalous emission of the Eu^{2+} bound exciton.

From the above discussion, we see that, in order to observe the intraion transition of Eu^{2+} in the ZnS:Eu systems, we need to raise the edge of the conduction band above the first excited state of Eu^{2+} . This may be realized in ZnS:Eu^{2+} nanoparticles. Due to quantum confinement, the energy gap opens up, the conduction band moves to higher energy, and the valence band moves to lower energy. The extent to which each band moves depends on the relative values of the effective mass of electron (m_e^*) and hole (m_h^*). According to the effective-mass approximation model,¹²⁻¹⁴ the increase of the energy gap is ~ 1.07 eV for a 2.5-nm-sized ZnS nanoparticle. For ZnS , m_e^* and m_h^* are $0.25m_e$ and $0.59m_e$,^{13,14} respectively. In this case, the edge of the valence band moves down by ~ 0.32 eV, while the edge of the conduction band moves up by ~ 0.75 eV. Consequently, the conduction-band edge is about 0.30 eV above the first excited state of Eu^{2+} . Similarly, the conduction-band edge is about 0.12 eV higher than the first excited state level of Eu^{2+} in a 3-nm-sized particle, and is almost at the same level as the first excited state of Eu^{2+} in a 3.5-nm-sized particle (see Fig. 6). If the edge of the conduction band is higher than the first excited state of Eu^{2+} , the energy required for intraion excitation is smaller than that for the photoionization transition, and the intraion transition may occur. Accordingly, we can predict that the intraion transition of Eu^{2+} can be observed in a ZnS:Eu nanoparticle smaller than 3.5 nm.

The characteristic energy structure of the nanostructured system can explain why the energy transfer from nanosized ZnS host to Eu^{2+} ions is so efficient. In ZnS:Eu^{2+} nanostructures, the $4f^7$ ground-state level of Eu^{2+} lies in the forbidden gap, and the first $4f^6 5d^1$ excited state lies fairly close to the

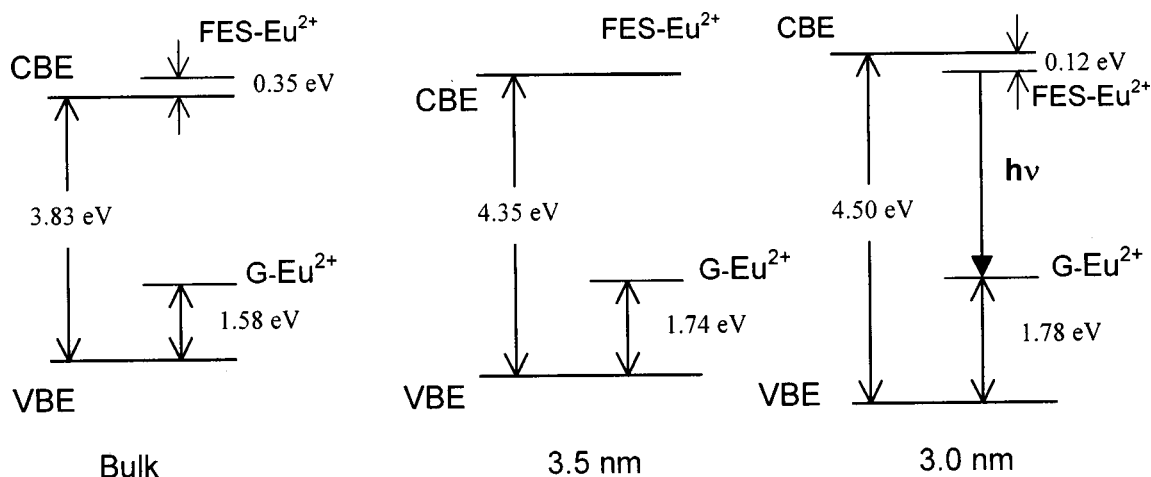


FIG. 6. Energy structure scheme of bulk (left) and nanophase ZnS:Eu²⁺ of 3.5 (middle) and 3.0 nm (right). In the bulk, the first excited state (FES) of Eu²⁺ is ~ 0.35 eV above the edge of the conduction band (CBE) in bulk ZnS (Ref. 5), the excited states of Eu²⁺ are degenerate with the continuum of the conduction band. Photoionization easily occurs and no intraion transition could be observed. The CBE of ZnS is about 0.12 eV higher than the FES of Eu²⁺ in a 3-nm-sized particle. In this case the intraion transition of Eu²⁺ becomes possible. For a 3.5-nm-sized particle, the CBE of ZnS is almost at the same level as the FES of Eu²⁺. This suggests that the intraion transition of Eu²⁺ can be observed in ZnS:Eu²⁺ nanoparticles smaller than 3.5 nm. G-Eu²⁺ stands for the ground state of Eu²⁺, the VBE is the edge of the valance band of ZnS.

edge of the conduction band of ZnS. Since the wave functions of conduction electrons in ZnS are *d* like, it is expected that the $4f^65d^1$ excited state of the Eu²⁺ ions will interact strongly with the conduction electrons. This interaction will result in an efficient energy transfer from the nanosized ZnS host to the Eu²⁺ emitter, and thus make Eu²⁺-doped nanosized ZnS an efficient phosphor.

In summary, we have observed the luminescence of Eu²⁺ in ZnS:Eu nanoparticles. The luminescence of Eu²⁺ from indirect excitation of the host is much stronger than that from direct excitation of Eu²⁺. The energy scheme of Eu²⁺ in nanostructured ZnS is different from that in bulk ZnS. Due to quantum confinement, the band gap opens up and the edge of the ZnS conduction band moves to a higher energy than the

first excited state level of Eu²⁺, and thus enables the intraion transition of Eu²⁺ ions.

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