Study on the Luminescence Properties of ZnS:Mn$^{2+}$ Particles by High Temperature Solid Phase Method

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Abstract. ZnS has attracted wide attention for its potential applications in optoelectronic fields, such as solid-state lighting, fluorescent probes, electroluminescent devices and field emission displays. In this work, Mn$^{2+}$-doped ZnS with hexagonal structure were prepared by high temperature solid phase method using MnCO$_3$ as manganese source, and the effect of Mn$^{2+}$ doping on ZnS was studied. The results show that the particle shape of ZnS doped with Mn$^{2+}$ is hexagonal structure, Mn$^{2+}$ doping changes the position and intensity of ZnS absorption spectrum and photoluminescence band. The absorption peak at 340 nm progressively moves to the right as Mn$^{2+}$ doping rises, a new conspicuous absorption peak forms in the visible area, and the maximum photoluminescence intensity of ZnS:Mn$^{2+}$ steadily increases. However, when the Mn$^{2+}$ doping exceeds the ratio of 4at.%, the photoluminescence intensity showed a decreasing trend. This indicates that the number of effective emission centers reaches the maximum when the doping concentration of Mn$^{2+}$ is the most suitable.

Keywords. ZnS; doping; sintering additives; photoluminescence.

1. Introduction

At ambient temperature, ZnS has a band gap of roughly 3.5-3.7 eV and a free exciton binding energy of 3.8 MeV, constituting it a typical II-VI semiconductor material. It has good ferromagnetic, piezoelectric, photoelectric and photosensitive properties. Due to its high specific surface area and quantum size effect, ZnS is often used as an important matrix material for polychromatic phosphors because of its high quantum effect in electroluminescence and photoluminescence [1-4].

ZnS has two kinds of crystal structures, namely sphalerite structure ($\beta$-ZnS) and wurtzite structure ($\alpha$-ZnS). The $\beta$-ZnS can exist stably at room temperature, while the $\alpha$-ZnS is generally formed by the phase transition of $\beta$-ZnS, and the phase transition temperature is about 1020°C. The difference of the atomic arrangement in the microstructure of the two kinds of crystalline ZnS makes the properties have great differences. For example, $\alpha$-ZnS has a larger band gap width than $\beta$-ZnS, and the luminescence properties of $\alpha$-ZnS are much higher than that of $\beta$-ZnS [5].

Many scholars introduce Sm$^{3+}$, Cu$^{2+}$ and Ni$^{2+}$ doping into ZnS, as a result of which new energy levels are generated in the band gap, which changes the microstructure, defects and energy band properties of ZnS matrix, thus improving the optical properties of doped ZnS. In general, ZnS doped Sm$^{3+}$ emits red light [6], doped Ni$^{2+}$ emits green light [7], and doped Mn$^{2+}$ emits orange-yellow light [8]. Tan et al. [9]...
successfully doped Sm$^{3+}$ into ZnS quantum dots using wet chemical methods. They found that the photoluminescence intensity of ZnS rose as the Sm$^{3+}$-doped content rose from 0.5 to 3.0%, and declined as the Sm$^{3+}$-doped content increased above 3%, which was related to the cross-relaxation energy transfer between Sm$^{3+}$ ions. Yang et al. [10] prepared ZnS: Ni$^{2+}$ nanoparticles by chemical co-precipitation method with nickel salt compounds as Ni source. The results demonstrate that when the appropriate doping mole ratio of Ni$^{2+}$ is 0.3%, ZnS nanoparticles doped with Ni$^{2+}$ exhibit a prominent green emission band at 520 nm, and the fluorescence quantum yield is much greater than pure ZnS crystals. Quan et al. [11] studied the luminescence properties of nanometer ZnS: Mn$^{2+}$ doped with Mn$^{2+}$, and adjusted the number of luminescence centers by controlling the doping content of Mn$^{2+}$. At present, it has been recognized that the semiconductor quantum dots doped with Mn$^{2+}$ have high emission efficiency and long emission decay life (μs to ms) [12-14]. However, the study on the luminescence principle of Mn$^{2+}$-doped ZnS, the optimal doping ratio and the optimization of preparation technology are not enough.

In this paper, ZnS luminescent particles were prepared by high temperature solid phase method, and the effects of Mn$^{2+}$ doping on the microstructure, light absorption characteristics and luminescent properties of ZnS were studied.

2. Experimental

ZnS: Mn$^{2+}$ luminescent particles were prepared by high temperature solid-phase sintering method using ZnS (ZnS, 99.99%), manganese carbonate (MnCO$_3$, 99.95%), anhydrous ethanol (CH$_3$OH, 99.70%) and high purity nitrogen (N$_2$, 99.99%) as raw materials. The addition amounts of Mn$^{2+}$ were 2at.%, 4at.%, and 6at.%, respectively. The raw material was weighed in proportion and mixed with adequate amount of anhydrous ethanol to form slurry. The resulting slurry was continuously dried at 80℃ in a drying oven until the anhydrous ethanol was completely volatilized. This mixture was put into the corundum porcelain boat and sintered in a tube furnace at 1050℃ for 4 h. The tube furnace warmed up at a rate of 5℃ per minute. Throughout the sintering process, N$_2$ was fed into the tube at a rate of 20 ml/min. Wait until the high temperature solid sintering was complete, the samples were taken and placed in an agate mortar. The powdered samples were ground and sieved into fine particles.

The crystalline structure of the samples was studied using the X-ray diffractometer (XRD, D/max2500PC, Japan). The surface morphology was examined by a field emission scanning electron microscope (SEM, FEINovaNano450). The absorption spectra of the samples in the ultraviolet were measured by UV-visible spectrophotometer (UV2600, Japan). The sophisticated steady-state transient fluorescence measuring device was used to capture the photoluminescence (PL) spectra.

3. Results and Discussion

3.1. The Crystal Structure and Micromorphology of ZnS: Mn$^{2+}$

Figure 1 shows XRD patterns of ZnS and ZnS: Mn$^{2+}$ samples. As can be seen from curve, the characteristic peaks of the ZnS raw material sample at $2\theta = 28.59^\circ$, 33.35°, 47.57° and 56.40° are exactly in line with the peak positions on the PDF CARDS of β-ZnS (111), (200), (220) and (311). It shows that the ZnS raw material is β-ZnS with cubic crystal structure. After sintering at 1050℃ for 4h, the positions of some characteristic diffraction peaks in XRD pattern are consistent with those on PDF card of α-ZnS. Crystallographic characteristic peaks of (100), (002), (101), (102), (110), (103) and (112) hexagonal phases in curves II and III. A small impurity peak at 33° was observed in sample II, which may be attributed to cubic ZnS. Therefore, we judged that the phase transition of ZnS was incomplete. This may be due to the small amount of Mn$^{2+}$ doping and the almost equal ionic radius of Mn$^{2+}$ (0.89 Å) and Zn$^{2+}$ (0.88 Å).

The micromorphology of the ZnS: Mn$^{2+}$ samples is depicted in figure 2. After sintering, the particle
shape of ZnS doped with Mn$^{2+}$ is inclined to hexagonal structure.

![Figure 1. XRD patterns of samples.](image1.png)

![Figure 2. Micromorphology of α-ZnS doped with 4 at. % Mn$^{2+}$.](image2.png)

The particle size distribution of ZnS:Mn$^{2+}$ can be seen in figure 3. The typical particle size is roughly 4 μm, as seen in the graph.

![Figure 3. Particle size distribution of ZnS:Mn$^{2+}$.](image3.png)

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The EDS spectra of ZnS:Mn$^{2+}$ is illustrated in figure 4. It can be seen from the element distribution spectrum that the particles in the scanning area contain a small amount of Mn in addition to the S and Zn that the ZnS particles should have. This result matches the element types contained in ZnS:Mn$^{2+}$ particles, indicating that Mn element is doped into ZnS crystal cells.

3.2. Effect of Mn$^{2+}$ Doping on the Light Absorption Properties of ZnS

Figure 5 shows the UV-Vis absorption spectra of ZnS and ZnS:Mn$^{2+}$ samples. It can be seen from the figure that pure α-ZnS and β-ZnS have only one absorption peak in the UV area at around 340 nm, and no absorption peak is observed in visible range (390-780 nm). This is because the wavelength of visible light is long and the energy carried by photons is low, which cannot reach the energy needed for electron transition from valence band to conduction band. Since pure ZnS particles only absorb ultraviolet light,
the fluorescence recovery ability of ZnS in photoluminescence will be affected, and its application range will be limited.

There are many obvious absorption peaks for Mn²⁺-doped ZnS on the spectrum, among which two tiny absorption peaks near the wavelength of about 500 nm, and a new absorption peak is found at the visible light with a wavelength of 730 nm, as shown in figure 5. The absorption intensity of ZnS:Mn²⁺ in the visible light spectrum rises as Mn²⁺ doping increases, which might be owing to a combination of quantization and defect states in the lattice structure generated by differing Mn²⁺ and Zn²⁺ ion sizes [15]. The edge of the absorption peak at 340 nm progressively changes to the right as the Mn²⁺ doping level increases, as seen in the figure. The direct energy transfer between the semiconductor-excited state and the Mn²⁺ 3d levels causes this shift [15].

3.3. Effect of Mn²⁺ Doping on Photoluminescence Properties of ZnS

Figure 6 shows the PL spectra of samples when excited by a light source with a wavelength of 320 nm.
The α-ZnS showed one green emission band at about 530 nm, and a wide yellow-orange emission band of α-ZnS:Mn²⁺ at 580 nm arises in the PL spectra.

The luminescence principle and the change mechanism of the luminescence peak position are shown in figure 7. When electrons in ZnS are stimulated by external energy (E), the electrons are stimulated to transition from the valence band to the conduction band, and the recombination of electrons and holes in conduction band leads to the release of energy. Energy is released in two ways. When released in the first way, as shown in figure 7, green light of wavelength λ₁=530 nm is emitted, which is the luminescence mechanism of α-ZnS. When energy is released in the second way, the transfer of energy to Mn²⁺ makes the extranuclear electrons of Mn²⁺ transition from ground state to high energy state. But high energy states are unstable, so electrons tend to return to ground state of low energy. The process of electron transition is accompanied by the release of energy in the form of light. Finally, the photoluminescence spectra, which peaked near 580 nm, showed an efficient typical orange-yellow emission from the ⁴T₁ to ⁶A₁ transition of the Mn²⁺.

![Figure 6. PL spectra of α-ZnS and ZnS:Mn²⁺.](image)

![Figure 7. Luminescence principle of ZnS:Mn²⁺.](image)

4. Conclusions
In summary, Mn²⁺-doped ZnS with hexagonal structure were successfully prepared by high temperature solid phase method. Mn²⁺ doping changes the position and intensity of ZnS absorption spectrum and photoluminescence band. With the increase of Mn²⁺ doping, the absorption peak at 340 nm gradually shifts to the right, a new obvious absorption peak appears in the visible region of 730 nm, and the maximum photoluminescence intensity of ZnS:Mn²⁺ increases gradually. When excited by a light source with a wavelength of 320 nm, a wide yellow-orange emission band of α-ZnS:Mn²⁺ at 580 nm arises in the photoluminescence spectra. The Mn²⁺ is the luminescence center through the electron transition from ⁴T₁ to ⁶A₁.

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