Preparation and Optical Characterizations of Manganese Doped Zinc Sulfide Nanoparticles

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In 1994, Bhargava et al. reported for the first time that manganese doped zinc sulfide nanocrystals were synthesized by chemical process, which have high efficiency of photoluminescence and ultrafast electron-hole recombination rate [1]. These spectacular results suggest that doped semiconductor nanocrystals form a new class of luminescence materials, with a wide range of potential applications in displays or lasers. Since then, many scholars have researched on the luminescence of various doped nanocrystals and the potential application of these luminescent materials.

Doped zinc sulfide with manganese is usually synthesized by thermal diffusion of Mn salt at high temperature (>1100℃). Nanocrystals will coagulate easily and melt at a reduced temperature in the thermal diffusion, which makes that the diameter of crystals will be higher and the range of particle size will be wider. So the synthesis of nanoparticles is a new emerging field in solid-state chemistry. There are several methods to synthesize doped nanocrystals, such as matrix-mediated growth technique, coating method, sol-gel system recently. In this article, we report our progress in preparation of Mn doped ZnS nanocrystals by microemulsion system and their optical characterization at room temperature.

ZnS:Mn nanoparticles were prepared by microemulsion method. A detailed description of the synthesized procedure is presented elsewhere [2].

By the transmission electron microscopy (TEM) and dynamic light scattering (DLS), it can be seen that the particle size range from 3 to 11 nm, and the size distribution of ZnS:Mn nanoparticles is relatively narrow. The crystalline structure of the ZnS:Mn nanoparticles is characterized by the XRD technique. There are three peaks in this figure, which are at 28.9°、48.2° and 56.3°corresponded to 111、220 and 311 planes of cubic zinc sulfide respectively. And we have observed that ZnS:Cu nanoparticles prepared by the same microemulsion system have also the same crystalline structure [2].

The peak in the UV absorption is indicative of the bandgap of the semiconductor ZnS particles. The bulk ZnS absorption peak is expected at 340.6nm (E_g=3.65eV). The curves demonstrate that the bandgap of the materials shift towards higher wavelengths compared to the bulk ZnS materials.

From excitation spectrum, the excitation peaks of nanoparticles are at 285.5nm、287nm、291.5nm and 296nm respectively. In bulk ZnS:Mn ,the excitation has its maximum at 332nm. This excitation wavelength is closed to the bandgap of bulk ZnS (340nm). The Mn excitation in the ZnS:Mn nanoparticles has its maximum intensity at a wavelength 285.5nm (4.35eV), in which UV absorption peak is at 283nm. In spite of the variation between the two values, it is clear that the changes in the excitation energy of the Mn^{2+} transition is due to the increased bandgap of ZnS:Mn particles. With the diameter of ZnS:Mn nanocrystals increased, the bandgap of materials becomes higher, as well as the blue shift of the excitation peaks changes larger.

Emission measurements demonstrate the effects of doping the ZnS with Mn. The emission peaks of materials are at 585～595 nm, which is due to the luminescence of Mn^{2+} in ZnS. The energy transfering from ZnS to Mn^{2+} results in the luminescence of Mn^{2+}. The excitation bandgap of ZnS forms excitons, and these excitons get the center of Mn^{2+} through nonradiation dominates, by means of the transition of $^4T_1–^6A_1$ luminescence. This spectrum is evidence that Mn^{2+} has been incorporated into the ZnS nanoparticles. In addition, the emission spectrum of materials shows the red shift with respect to bulk ZnS, however the shift is slight. The red shift of peak position is thought to be a result of e−h localization in the quantum-confined particles lifting the degeneracy of the $^4T_1$ and $^6A_1$ levels and thereby shifting the transition to lower energy levels.

References

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2. Y. Zhang, L. Li, J. Materials Engineering, 212 (2001) 31

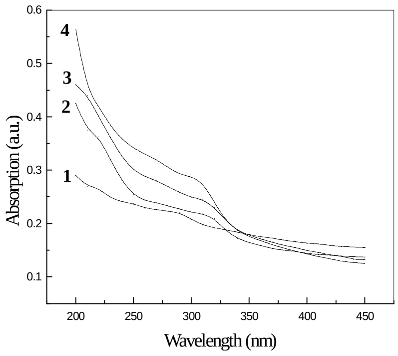

Fig. 1. UV absorption of ZnS:Mn nanoparticles

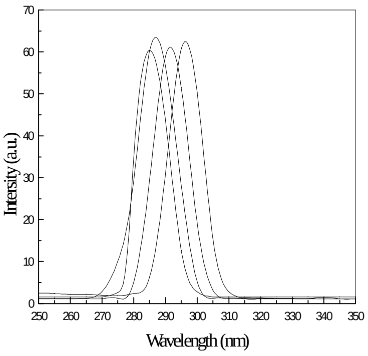

Fig. 2. Excitation spectrum of ZnS:Mn nanoparticles

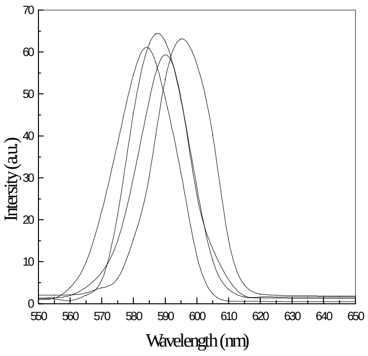

Fig. 3. Emission spectrum of ZnS:Mn nanoparticles