Study of optical properties of manganese doped ZnS nanocrystals

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Abstract

ZnS:Mn nanocrystals were prepared by the coprecipitation method. The reaction conditions, such as the amount of manganese doped, the concentration of the reactant, the surfactant, the reactive temperature and time were studied systematically. Nanocrystalline powders and sols exist. The photoluminescent excitation spectra and the photoluminescence spectra of ZnS:Mn nanocrystal were studied by the fluorescent divide spectroscopy under an ultraviolet excitation. It is shown that the luminescent sites of the nanocrystalline powder and sol are different from that of ZnS:Mn bulk crystal. The luminescent site of the sample results from the transition of the doped Mn^{2+} in the ZnS crystal.

1. Introduction

The luminescent efficiency of ZnS matrix is very high. Its preparation technology is simple and the cost is low. It has great practical value. The manganese doped ZnS (ZnS:Mn) bulk materials have been extensively studied by many authors [1,2], but very little work [3,4] has been carried out for the nanocrystalline materials. When the manganese was doped into ZnZ, the Mn^{2+} ions replace zinc ions and the optical properties of ZnS bulk material and the luminescent sites changed. The optical properties of ZnS:Mn nanocrystals are studied in this paper.

The ZnS:Mn nanocrystals were prepared by the coprecipitation method. Bulk ZnS is usually doped with manganese by thermal diffusion at high temperature (> 1100 °C). Since the nanocrystallites sinter at a much lower temperature, they must be doped during precipitation. The reaction conditions, such as the amount of manganese doped, the concentration of the reactant, the surfactant, the reactive temperature and time were studied systematically. Through a large number of experiments, the best reactive conditions were selected. The samples used in this study have two forms: powders and colloids. The coprecipitate was centrifuged, washed and dried and the precursor of the ZnS:Mn nanocrystal was prepared. The precursor was calcined at 200–700 °C for 2 h to

form ZnS:Mn nanocrystal. The particle diameter of ZnS:Mn nanocrystals sol with the surfactant is about 5 nm and the diameter of the powder calcined at 400 °C with the surfactant is about 12 nm. The structural properties of nanocrystal were then examined by X-ray diffraction (XRD) and infrared spectroscopy (IR). It was found that ZnS:Mn nanocrystal size increases with increasing calcined temperature.

The optical properties were characterized by fluorescent divide spectroscopy (FDS) under an ultraviolet excitation using a Hitachi F-4000 spectrometer. Both the excitation and luminous spectra of the samples were measured by FDS.

The Mn^{2+} ion has $3d^5$ configuration, which gives rise to a $^6S_{5/2}$ ground state in a tetrahedral crystal field. The first excitated state of gaseous Mn^{2+} is ^4G. By the parity selection rule, the crystal-field (CF) transition is parity forbidden. When Mn^{2+} ions are doped into the ZnS crystal, it replaces an amount of Zn^{2+}, and the ^4G of the first excitated state of Mn^{2+} in tetrahedral symmetry, T_d, has been split. Because of the crystal-field disturbance, the effect of other ions around on electric constructure of Mn^{2+} ion has relieved some forbidding. Then, the crystal field transition of Mn^{2+} is dependent strongly on its host nanocrystal.

ZnS crystal is semi-conductor material with an energy band gap of 3.6 eV [5]. Because the photon with thermal equilibrium fills up, the effective energy band gap is 339 nm at room temperature. With its energy band characteristic, ZnS becomes good host material.
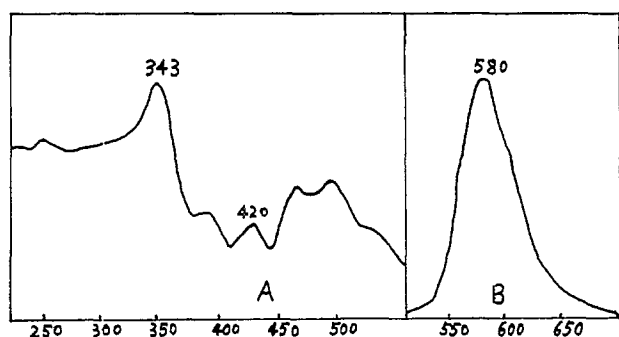
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Fig. 1. The luminescent excitation (PLE) spectra (a) and the photoluminescence (PL) spectra (b) of ZnS:Mn bulk powder.
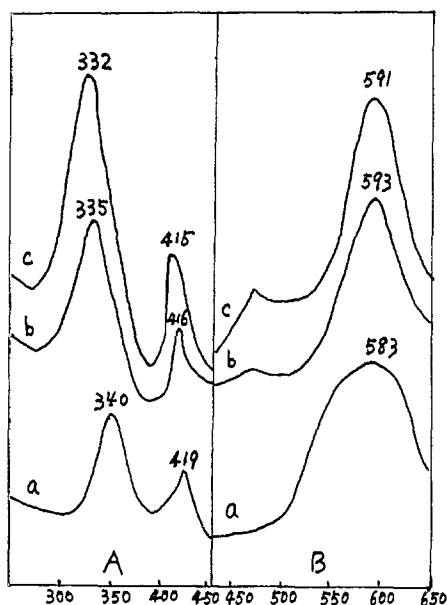

Fig. 2. The luminescent excitation (PLE) spectra (a) and the photoluminescence (PL) spectra (b) of ZnS:Mn nanocrystalline powder.

ZnS:Mn material is ZnS semiconductor crystal doped with manganese impurities. The Mn^{2+} ion d-electron states acts as efficient luminescent centers while interacting strongly with the S-P electric state of the host crystal into which external electronic excitation is normally directed. This yellow emission observed in this photoluminescence of bulk Zns:Mn is associated with the $^4T_1 \rightarrow {}^6A_1$ of Mn^{2+} ion transition and its peaks at around 2.12 eV (585 nm) with a half width of 0.23 eV at room temperatures [6].

Fig. 1 is the photoluminescent excitation (PLE) spectra (a) and the photoluminescence (PL) spectra (b) of ZnS:Mn bulk powder calcined at high temperature (1100 °C) by the physical method. From Fig. 1, the PLE peaks are many and the highest peak is at 343 nm. The PLE (a) and PL (b) data for ZnS:Mn prepared by the chemical method are shown in Fig. 2. When Fig. 2(a) is compared with Fig. 1, it is found

that the PLE and PL peaks are very similar. It is shown that the sample calcined at high temperature by the chemical method may behave like bulk materials. The PLE spectra of ZnS:Mn nanocrystalline powders in Fig. 2(b) and (c) are different from that of ZnS:Mn bulk material. We know that the highest energy peak in the PLE spectra of nanocrystals is indicative [4]. This is consistent with the observation that in a given sample, the peak of the PLE spectrum shifts to higher energy under UV exposure. Then, the size of the PLE peak may behave like the particle size of ZnS:Mn nanocrystal. The particle size of the sample with 332 nm excitative peak is the smallest in the three samples. The PL peak of the Mn^{2+} transition in Fig. 2(a) is 583 nm, which is similar to that of ZnS:Mn bulk crystal. The energy band of the luminescent spectrum decides the luminescent site of the samples. Because the luminescent energy bands of the two samples are similar, it is shown that these luminescent sites are the same, too.

The samples in Fig. 2(b) and (c) are all ZnS:Mn nanocrystal, which are without and with the surfactant. In the reactive system, the function of the surfactant is that a protected film of high molecular compound is formed on the surface of the samples and results in the passivation on the surface of ZnS:Mn nanocrystals. In addition, the surfactant makes the ZnS:Mn particle divide and decreases the action between each particle and the particle size increased. The PLE peak of powders with the surfactant is compared with that of samples without the surfactant; the PLE peak of samples with the surfactant obviously decreases. This may be owing to the passivation of surface on the nanocrystal and the photopolymerization of the surfactant. It is shown that the surfactant plays a protection role on the nanocrystal. The PL peaks of Mn^{2+} in the nanocrystal without and with the surfactant are at 591 and 592 nm, respectively. It is shown that the luminescent sites are the same and different from that of the sample calcined at high temperature. It is also shown that
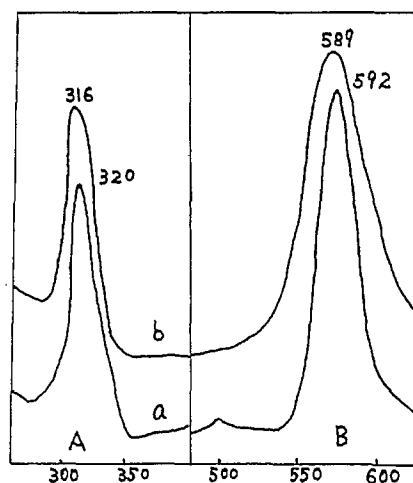

Fig. 3. The luminescent excitation (PLE) spectra (a) and the photoluminescence (PL) spectra (b) of ZnS:Mn nanocrystalline sol.

the luminescent site of the Mn-doped ZnS nanocrystals is different from that of ZnS:Mn bulk crystal.

Fig. 3 is the PLE and PL spectra of ZnS:Mn sol without (a) and with (b) the surfactant. These results are similar to those of ZnS:Mn powder. Adding the surfactant in the sol, the PLE peaks decreased, however the particle size of the sol decreased. From Figs. 2 and 3, the PLE peaks of the sol are smaller than that of nanocrystalline powders. It is shown that the particle size of the sols are smaller than that of the powders. However, the luminescent sites of the sol with and without the surfactant are the same as that of nanocrystalline powder and are different from that of bulk ZnS:Mn crystal.

In conclusion, the luminescent sites of the nanocrystalline powder and sol are different from that of the ZnS:Mn bulk crystal. The luminescent site of the sample results from the transition of the doped Mn^{2+} in the ZnS crystal.

Acknowledgements

References

[1] J. Tanaka, K. Suto, H. Kubayashi and H. Sasakura, *Jpn. J. Appl. Phys., 15* (1976) 2359.
[2] Y. Wang and N. Herron, *J. Phys. Chem., 95* (1991) 525.
[3] R.N. Bhargava and D. Gallagher, *Phys. Rev. Lett., 72* (1994) 416.
[4] Y. Wang and N. Herron, *Solid State Commun., 77* (1991) 33.
[5] L. Brus, *J. Quantum Electron, 22* (1986) 1909.
[6] L. Brus, *J. Phys. Chem., 90* (1986) 2555.