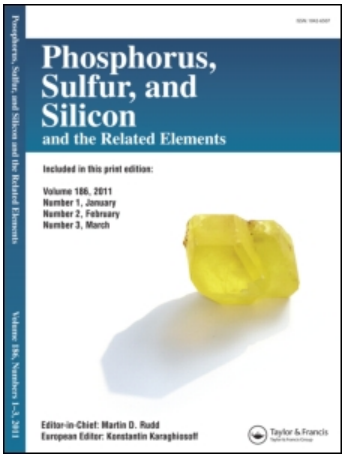

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POLY(MAA-Mn) FOR TRIPLE-LAYER STRUCTURE SYNTHESIS OF ZnS/ZnS:Mn/SiO_2 PHOSPHORS

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Methacrylic acid (MAA) was used as a manganese carrier to prepare ZnS/MAA-Mn particles, and ZnS/ZnS:Mn phosphors were formed from ZnS/MAA-Mn by ion substitution through heat treatment. After silica coating on surface by chemical precipitation method with tetraethyl orthosilicate (TEOS), ZnS/ZnS:Mn/SiO_2 phosphors were prepared successfully as a new core/shell structure compound. The thickness of layers was controlled by adjusting concentrations of manganese (II) acetate ($Mn(CH_3COO)_2$) and TEOS. Structure, morphology, and composition of prepared phosphors were investigated by X-ray diffraction (XRD), transmission electron microscope (TEM), and X-ray photoelectron spectroscopy (XPS), respectively. Photoluminescence (PL) properties of ZnS with different Mn^{2+} content were analyzed by PL spectrometer. PL emission intensity and PL stability were analyzed for evaluating effects of silica coating and Mn^{2+} activator doping. As a result, the structure of two layers could be observed, and optimum composition of ZnS/ZnS:Mn/SiO_2 structure was also obtained.

Keywords Ion substitution; MAA; photoluminescence; silica coating; XPS; ZnS phosphor

INTRODUCTION

Due to the unique physical properties of semiconductor materials, especially such as zinc sulfide (ZnS), they have been widely studied in recent years both from fundamental and applied points of view.[1,2] Because ZnS is a kind of wide band gap II–VI compound semiconductor material ($E_g \sim 3.6$ eV), and with its energy band characteristic, ZnS becomes a good host material.[3] Metal ions such as Cu, Pb, Eu, and Tb doped ZnS nanomaterials have been investigated for emission shift.[4–8] Many groups also have prepared ZnS:Mn particles by simple co-precipitation method,[9–11] but in fact, because the equilibrium constant of MnS is larger than that of ZnS, Mn^{2+} ions could not be easily doped into the lattice of ZnS by co-precipitation.[12] In order to get successful Mn^{2+} doped ZnS particles, an ion substitution method was priority-used to replace traditional methods in this article. The ion substitution method[13] is chosen for ZnS doped with Mn^{2+} ions by Mn^{2+} ions replacing partial sites of Zn in ZnS lattices, but maintaining ZnS lattice structure constantly. The process is that Mn^{2+} ions were coated on the surface of ZnS by carrier, and then taken part in an exchange reaction

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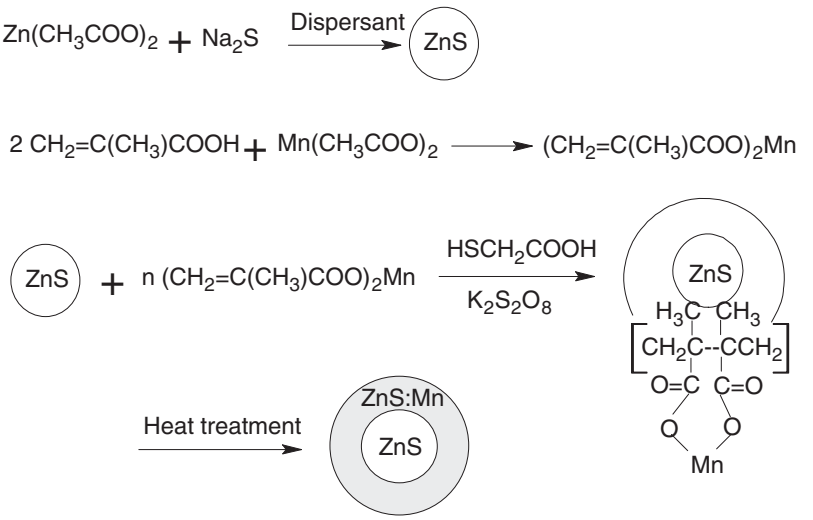

Figure 1 Reaction principle of formation of ZnS/ZnS:Mn core/shell structure.

with the surface Zn^{2+} ions by heat treatment. Another serious problem is that addition of Mn^{2+} ions decreases Zn vacancies in the ZnS lattices, which significantly inhibits the green emission intensity of the ZnS-based phosphor. In order to solve these serious problems, we designed new structure of the ZnS-based phosphor as a ZnS/ZnS:Mn/SiO_2 particle, which keeps both Mn^{2+} and Zn^{2+} ions emission with strong intensity by ZnS/ZnS:Mn core/shell structure and avoids Mn^{2+} ions decrease Zn vacancies in ZnS core. Also, silica coating on the surface of phosphor can improve luminescence stability, by restricting the effect of oxygen and other application environment on the phosphors.

In this article, according to reaction principle as shown in Figure 1, methacrylic acid (MAA) was chosen as a carrier of manganese to prepare ZnS/MAA-Mn particles, by which ZnS/ZnS:Mn phosphor of core/shell structure could be obtained after heat treatment. After silica coating by chemical precipitation method with tetraethyl orthosilicate (TEOS), ZnS/ZnS:Mn/SiO_2 phosphors were prepared successfully as a new core/shell structure compound. This synthetic process is described in the Experimental section in detail. By various analysis of performance test, the effect of raw materials ratio on structure and morphology of prepared phosphors was investigated, and effect of layer thickness on PL intensity and stability was also analyzed.

RESULTS AND DISCUSSION

XRD and XPS

In order to ensure synthesis of ZnS/ZnS:Mn/SiO_2 phosphors and the effect of silica coating on ZnS crystallinity, all XRD curves of phosphors were analyzed as shown in Figure 2, which exhibits a zinc-blended crystal structure. The three diffraction peaks correspond to (111), (220), and (311) planes of the cubic crystalline ZnS, respectively. After heat treatment, because MAA was destroyed, XRD intensity of sample became increased, which showed higher crystallinity of ZnS. According to the line width analysis of the (111) diffraction peak based on the Scherrer formula,[14] the average sizes of particles have been

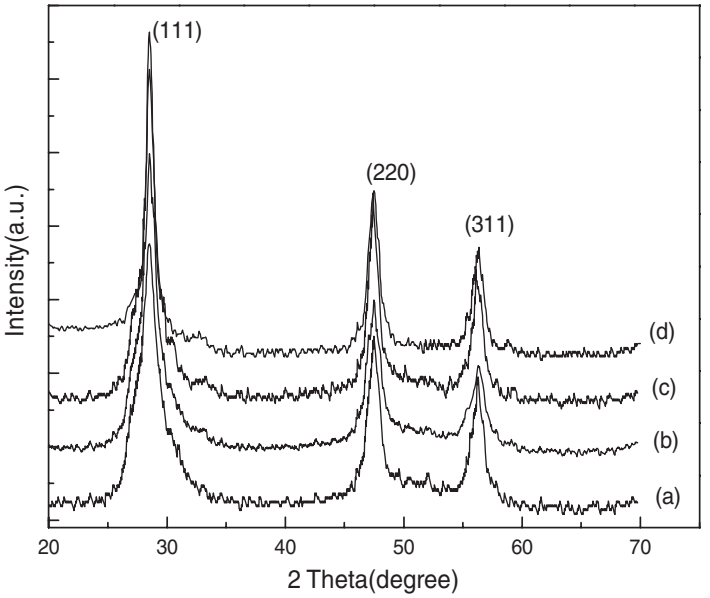

Figure 2 XRD pattern of (a) ZnS, (b) ZnS/MAA-Mn, (c) ZnS/ZnS:Mn, (d) ZnS/ZnS:Mn/SiO_2 samples.

estimated as 2–4 nm. Phosphors coated with silica did not show obvious new diffraction peaks (Figure 2d), which means there was no additional peak corresponding to amorphous silica.[15] Also, the MnS peak did not appear in XRD curves. For further investigation as to whether Mn ions exist or not in the prepared ZnS lattice, subsequent XPS analysis was executed.

Since XPS is a rather surface-sensitive technique, these spectra have revealed mostly the stoichiometry and chemical state of the outermost layers of the various particles.[16] Figure 3 shows XPS spectra of all particles. In the spectrum of sample (a), the obvious Zn (2p) peak at about 1022.4 eV and S (2p) peak at 162.7 eV revealed that the sample (a) was pure ZnS. From sample (b) spectrum, an additional Mn (2p) peak could be observed at about 645.1 eV, and this indicated that Mn successfully doped in sample, the outermost layer should be ZnS:Mn. Remarkable O (1s) appeared in both samples, which could be explained that O_2 or $-$OH was adsorbed on the sample surface, as no ZnO peak was detected by XRD. Typical Si (2p) peak at 103.0 eV and rapid decreases of Zn (2p), S (2p) peak intensity, respectively, (c) indicated that particles were coated with silica.

TEM and Zeta Potentials

Figure 4 shows TEM micrographs of ZnS/ZnS:Mn and ZnS/ZnS:Mn/SiO_2 particles. Figure 4a reveals the prepared ZnS/ZnS:Mn sample with an average diameter of about 55 nm. Phosphate groups formed polymeric chains and became attached to the metal ion as $PP^{2n-} + nM^{2+} \rightarrow$ MPP. After Na_2S was added, sulfur reacted with excess metal ions to form sulfide clusters. Clusters grew up by the coalescence of smaller clusters or on some metal ion seeds present in the solution. On a growing metal sulfide cluster, phosphate chains became attached through metal ions. And ZnS:Mn appeared on the surface of ZnS after heat treatment, so ZnS/ZnS:Mn was observed as a cluster that includes

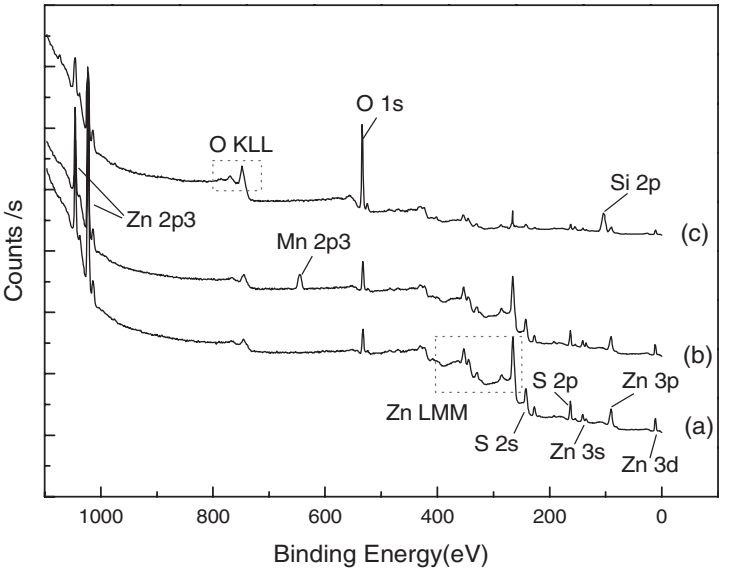

Figure 3 XPS pattern of (a) ZnS, (b) ZnS/ZnS:Mn, and (c) ZnS/ZnS:Mn/SiO_2.

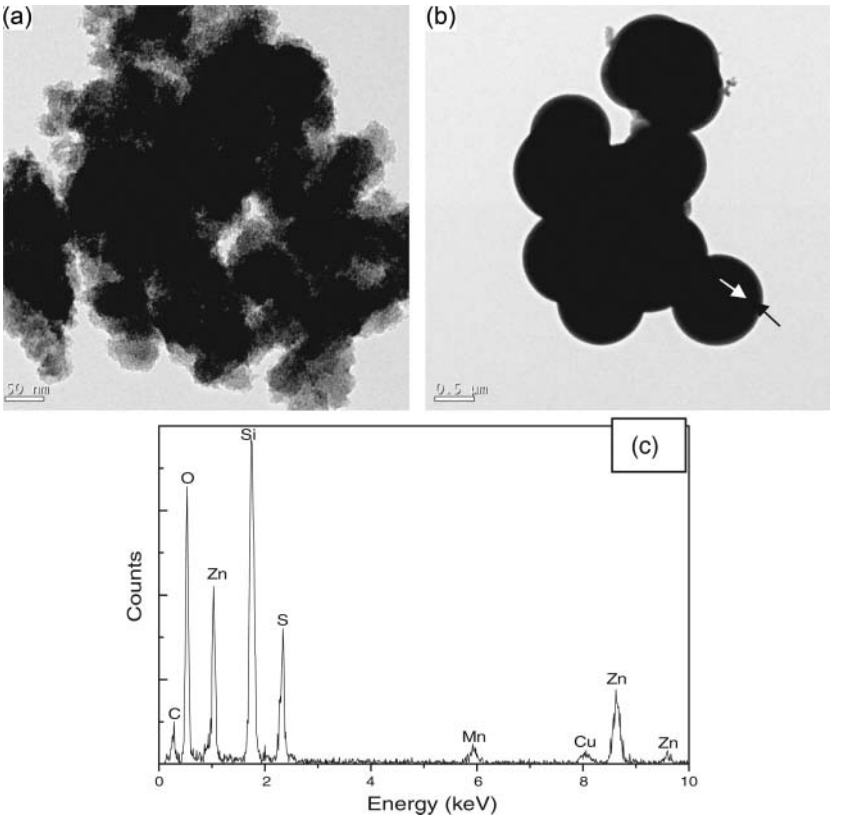

Figure 4 TEM images of (a) ZnS/ZnS:Mn, (b) ZnS/ZnS:Mn/SiO_2 particles, and (c) the corresponding EDX of ZnS/ZnS:Mn/SiO_2.

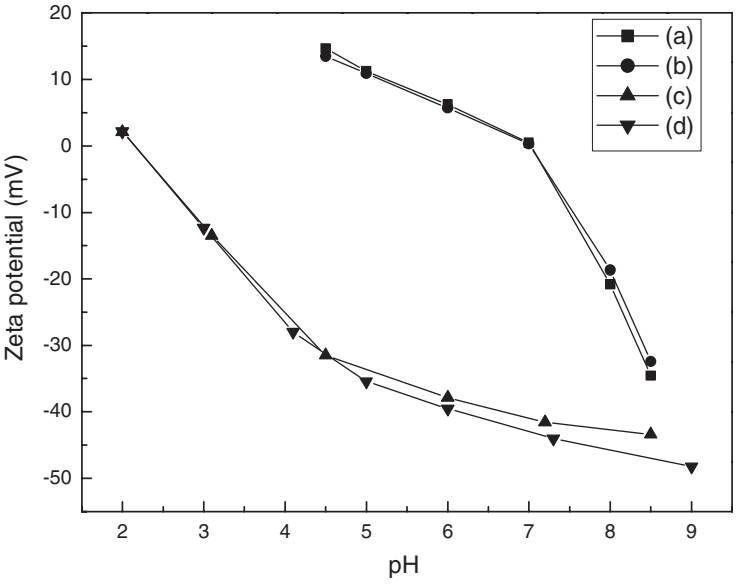

Figure 5 Zeta potentials of (a) ZnS, (b) ZnS/ZnS:Mn, (c) ZnS/ZnS:Mn/SiO_2, and (d) pure silica powders as the function of pH.

single particles. In Figure 4b, silica coating can be observed clearly on the outmost layer, which indicates that sulfide clusters were coated with silica and ZnS/ZnS:Mn/SiO_2 was successfully synthesized. The prepared particle size also obtained from Figure 4b was about 600 nm. The corresponding EDX of ZnS/ZnS:Mn/SiO_2 is shown in Figure 4c. All component elements of the compound were observed, which indicates that ZnS/ZnS:Mn particles were embedded in silica.

The zeta potentials for the uncoated, silica-coated phosphors, and silica powders were plotted against the medium pH as shown in Figure 5. Zeta potentials of uncoated powders against pH values shown in Figures 5a and 5b were quite different from silica-coated particles (Figure 5c) and pure silica (Figure 5d), because of different surface charge. The iso-electric point (IEP)[17] was changed from a pH of about 7.0 of the uncoated phosphors (Figures 5a and 5b) to pH about 2.0 for the silica-coated phosphors (Figure 5c). The zeta potential curve of ZnS/ZnS:Mn/SiO_2 was similar to that of pure silica, which means successful silica coating on phosphors. In the experimental process, the pH value was adjusted to about 5, which results in repulsive force among particles that has increased enough to improve dispersibility of phosphor powders, which will promote the coating process.[18]

Photoluminescence

Figure 6 shows the PL spectra of samples excited at 310 nm. It can be seen that the emission spectra were composed of two broad band peaks. The orange emission with its maximum at ~590 nm was caused by the transition from $4T_1$ (excited) to $6A_1$ (ground) of Mn^{2+} ions, indicating that the Mn^{2+} ions had been successfully incorporated into the ZnS host lattice. The blue emission peak centered at 401 nm was attributed to the self-activated Zn^{2+} vacancies in the lattice, which accompany a weak peak of S vacancies at about

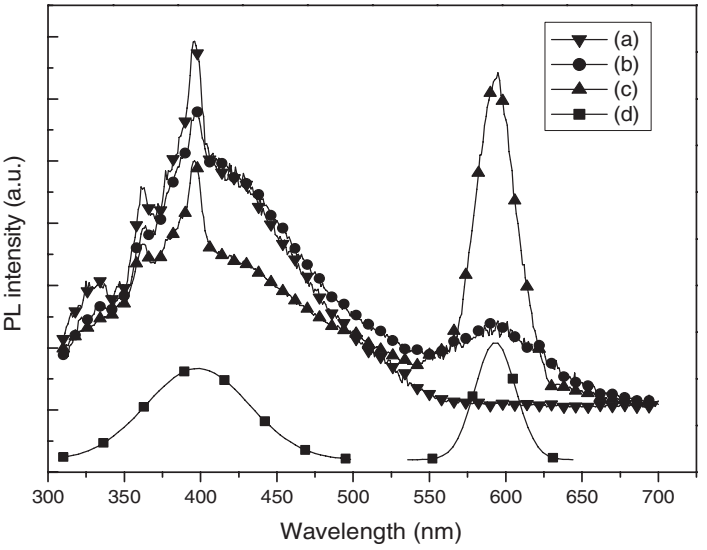

Figure 6 PL spectra of (a) ZnS, (b) ZnS/ZnS:Mn, (c) ZnS/ZnS:Mn/SiO_2 samples, and (d) Gaussian fitting of luminescence curves.

360 nm.[19] With the existence of Mn^{2+} luminescence centers, Zn^{2+} emission was observed strongly. The intensity of the 590 nm emission of the coated phosphors was about seven times that of uncoated phosphors, which means silica coating could significantly improve luminescence of phosphor. Because silica coating decreased the surface Mn^{2+} ions, which were so near to the quenching center, their luminescence can not be quenched easily, and result in luminescence enhancement.

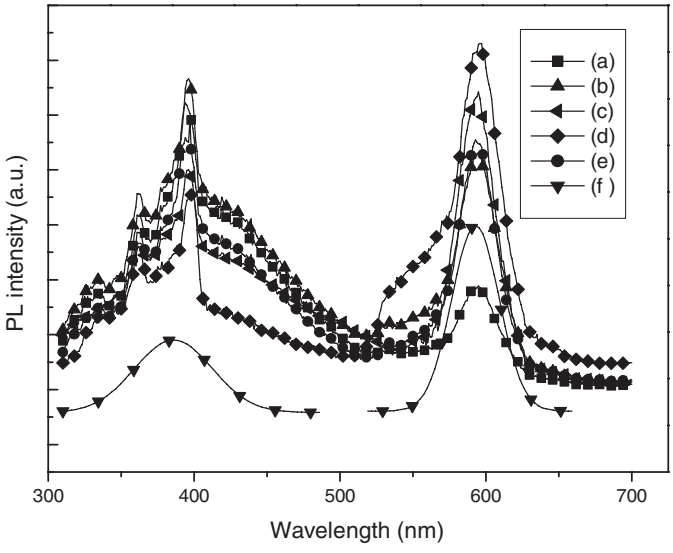

Figure 7 PL spectra of ZnS/ZnS:Mn/SiO_2 with different Mn^{2+} concentrations (a: 2%, b: 4%, c: 6%, d: 8%, e: 10%) and (f) Gaussian fitting of luminescence curves.

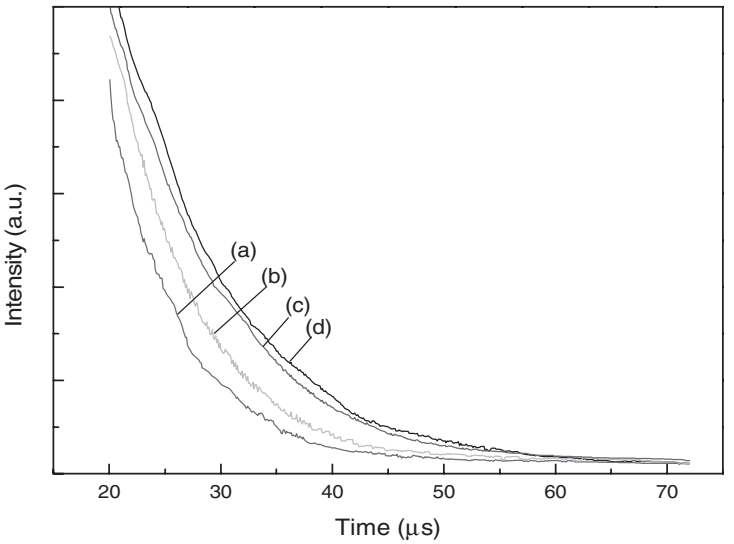

Figure 8 Decay curves of ZnS/ZnS:Mn/SiO_2 with different silica contents recorded at room temperature (a: 0%, b: 5%, c: 10.1%, and d: 18.7%).

PL spectra of ZnS/ZnS:Mn/SiO_2 with different Mn^{2+} concentration is shown in Figure 7. The spectra peak of ZnS/ZnS:Mn/SiO_2 was shifted from 592 nm to 598 nm with Mn^{2+} addition. Peak red-shift about 6 nm at higher Mn^{2+} concentration may be due to magnetic interactions between neighboring Mn^{2+} ions, and the emission peak of the magnetically coupled pair is observed to be red-shifted. As a result, the luminescence intensity increased with increasing the concentration of Mn^{2+}. Figure 7d showed the maximum values with 8% Mn^{2+} content. But when Mn^{2+} concentration increased over 8% (Figure 7e), emission intensity was showed to be rather decreased due to concentration quenching.[20,21]

Figure 8 shows decay time curves for ZnS/ZnS:Mn/SiO_2 phosphors. Here, excitations for both were carried out by using wavelength about 310 nm. Comparing with ZnS bulk materials, ZnS-based nanoparticles have short lifetimes because of quantum efficiency.[22] For a silica-coated sample, decay times of about 38.2 μs were obtained with 10% silica content, whereas in the case of ZnS/ZnS:Mn nanoparticles, decay time was about 27.6 μs. The luminescent lifetime become increasingly longer with the thickening of the silica shell. Usually, the surface Mn^{2+} ions act as nonradiative recombination centers, and the nonradiative recombination rate is very fast. Once the number of the surface Mn^{2+} ions is reduced by the silica shell, the nonradiative transition paths are blocked to some extent, leading to the slowing down of the luminescence decay.

CONCLUSION

By using MAA as a carrier of manganese, it was successful to prepare ZnS/MAA-Mn particles as intermediates for ZnS/ZnS:Mn phosphors. After silica coating by chemical precipitation with TEOS, the core/shell structure was synthesized successfully as a form of ZnS/ZnS:Mn/SiO_2. All obtained XRD curves of the samples proved that the ZnS crystal structure was formed. From XPS and EDX spectra, additional Mn peak indicated that Mn^{2+} successfully doped in the surface of ZnS as ZnS:Mn layer. Typical the Si peak also

could be obtained in the above spectra, which showed silica was coated on the surface of ZnS/ZnS:Mn, and this result also was proved by zeta potential curves. From TEM images, the silica layer could be observed clearly, which means successful synthesis of core/shell structure. By investigating photoluminescence of the samples, two obvious peaks from ZnS and Mn centers were observed from the spectrum of ZnS/ZnS:Mn/SiO_2. Intensity of coated phosphor was seven times more than that of the uncoated phosphors, and the lifetime of phosphor was improved effectively by silica coating. At last, optimum luminescence of ZnS/ZnS:Mn/SiO_2 phosphor was obtained with 8% Mn^{2+} content and 10% silica content.

EXPERIMENTAL

ZnS/ZnS:Mn/SiO_2 particles were prepared as follows: First, 0.01 mol $Zn(CH_3COO)_2$, 0.02 mol sodium acetate, and 0.005 mol sodium polyphosphate ($Na_5P_3O_{10}$) were dissolved in water (100 mL), and then appropriate freshly prepared Na_2S solution was added dropwise to the above mixture under vigorous stirring at room temperature. After 30 min, ZnS white precipitate was washed with distilled water. Second, $Mn(CH_3COO)_2$ and MAA were added into a beaker with solution temperature at 90°C, and stirring was continued for 2 h until $Mn(MAA)_2$ were formed adequately. Concentration of Mn^{2+} and MAA can be controlled by the content of raw materials and varied from 0 to 10% (molar ratio to Zn^{2+}). Third, pure ZnS was added to the $Mn(MAA)_2$ solution with stirring uniformly, and then appropriate aqueous solution of potassium persulfate and thioglycolic acid were added dropwise to the above mixtures at 80°C. After 1 h, prepared ZnS/MAA-Mn particles were cooled down to room temperature and separated from solution by centrifugation. And then these products were heat-treated for 1 h at 400°C under continuous argon flow, which stimulated Mn^{2+} ions doped into ZnS lattices by ion substitution. Subsequently, ZnS/ZnS:Mn phosphors were coated with silica by chemical precipitation method. TEOS as precursor was introduced to suspended phosphors solution, and then the mixtures were heated to 80°C and neutralized to pH 5.0 by diluted hydrochloride acid solution with stirring for 12 h. Last, coated phosphors were washed with distilled water and dried at 100 $\sim$ 110°C for 12 h.

The crystalline phase of the samples was determined by X-ray diffraction (XRD; Cu Kα, 40 kV, 60 mA, SIEMENS D/max-5000). The surface element composition of phosphors was analyzed by X-ray photoelectron spectroscopy (XPS; MultiLab 2000). Morphology and size of coated phosphors were observed by a transmission electron microscope (TEM; JEM-1010) with an energy-dispersive X-ray (EDX) spectroscope. Surface charges of samples were investigated with a Zeta Potential Instrument (ELS-8000, Otsuka Electronics Co.). The samples were dispersed into deionized water, and the pH of samples suspension is adjusted by adding very dilute hydrochloride acid solution or sodium hydroxide solution. Photoluminescence (PL) measurement was carried out at room temperature using 310 nm as the excitation wavelength with a Perkin Elmer LS-45 luminescence spectrometer.

REFERENCES

1. W. Wang, F. Huang, Y. Xia, and A. Wang, *J. Lumin.*, **128,** 610 (2008).
2. J. Yuan, C. Hao, and Z. Li, *Mater. Lett.*, **62,** 1782 (2008).
3. H. Hu and W. Zhang, *Opt. Mater.*, **28,** 536 (2006).
4. M. Wang, L. Sun, X. Fu, C. Liao, and C. Yan, *Solid State Commun.*, **115,** 493 (2000).
5. W.Q. Yang, L. Dai, L.P. You, and G.G. Qin, *Phys. Lett. A*, **372,** 4831 (2008).
6. A.A. Bol and A. Meijerink, *Phys. Stat. Sol. (b)*, **224,** 173 (2001).

7. H. Yang, L.X. Yu, L.C. Shen, and L. Wang, *Mater. Lett.*, **58,** 1172 (2004).
8. M. Ihara, T. Igarashi, T. Kusunoke, and K. Ohno, *J. Electronchem. Soc.*, **147,** 2355 (2000).
9. B. Steitz, Y. Axmann, H. Hofmann, and A. P. Fink, *J. Lumin.*, **128,** 92 (2008).
10. R. Pool, *Science*, **248,** 1186 (1990).
11. J. H. Park, S. H. Lee, J. S. Kim, H. L. Park, and S. D. Han, *J. Lumin.*, **126,** 566 (2007).
12. H. Song, Y. M. Leem, B. G. Kim, and Y. T. Yu, *J. Phys. Chem. Solid.*, **69,** 153 (2008).
13. A. A. Bol, R. V. Beek, and A. Meijerink, *Chem. Mater.*, **14,** 1121 (2002).
14. Y. T. Nien, K. H. Hwang, I. G. Chen, and K. Yu, *J. Alloys Compd.*, **455,** 519 (2008).
15. H. Song, Y. M. Leem, B. G. Kim, and Y. T. Yu, *Mater. Sci. Eng. B*, **143,** 70 (2007).
16. A. S. Ethiraj, N. Hebalkar, S. K. Kulkarni, and R. Pasricha, *J. Chem. Phys.*, **118,** 8945 (2003).
17. J. Yuan, C. Hao, and Z. Li, *Mater. Lett.*, **62,** 1782 (2008).
18. J. Yuan, K. Kajiyoshi, K. Yanagisawa, H. Sasaoka, and K. Nishimura, *Mater. Lett.*, **60,** 1284 (2006).
19. L. Cao, J. Zhang, S. Ren, and S. Huang, *Appl. Phys. Lett.*, **80,** 4300 (2002).
20. A. A. Bol and A. Meijerink, *J. Phys. Chem. B*, **105,** 10197 (2001).
21. L. Chen, J. H. Zhang, Y. S. Luo, S. Z. Lu, and X. J. Wang, *Appl. Phys. Lett.*, **112**(1), 84 (2004).
22. K. Yan, C. Duan, Y. Ma, S. Xia, and J. C. Krupa, *Phys. Rev. B*, **58,** 13585 (1998).