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## Sol-gel Synthesis and Characterization of Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> Spherical Core-Shell Particles

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The synthesis and characterization of  $Zn_2SiO_4$ :Mn phosphor layers on spherical silica spheres, i.e., core-shell particles of  $Zn_2SiO_4$ :Mn@SiO\_2 are described in this paper. First, monodisperse silica spheres with an average size around 750 nm have been obtained via the Stöber method by the hydrolysis and condensation of tetraethoxysilane  $Si(OC_2H_5)_4$  under base condition (using NH<sub>4</sub>OH as the catalyst). Second, the silica spheres are coated with  $Zn_2SiO_4$ :Mn phosphor layers by a sol-gel process. The resulting core-shell particles are characterized by X-ray diffraction, Fourier transform infrared spectroscopy, field emission scanning electron microscope, energy-dispersive X-ray spectroscopy, transmission electron microscopy, photoluminescence, low-voltage cathodoluminescence, as well as kinetic decay. The results confirm that the 1000°C-annealed sample consists of crystalline  $Zn_2SiO_4$ :Mn shells and amorphous SiO<sub>2</sub> cores with spherical morphology and narrow size distribution. The  $Zn_2SiO_4$ :Mn@SiO<sub>2</sub> particles show the green emission at 521 nm corresponding to  ${}^{4}T_1({}^{4}G)$ - ${}^{6}A_1({}^{6}S)$  transition of Mn<sup>2+</sup> under the excitation of UV (250 nm), vacuum UV (172 nm), and electron-beams (1–6 kV). The luminescence intensity has been studied as a function of coating number, accelerating voltage, and filament current, respectively.

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The core-shell composite particles are of extensive scientific and technological interest due to the ability to fine-tune their properties.<sup>1-5</sup> Core-shell materials consist of a core structural domain covered by a shell domain. The core and shell domains may be composed of a variety of materials including polymers, inorganic solids, and metals. The structure, size, and composition of these particles can be easily altered in a controllable way to tailor their magnetic, optical, mechanical, thermal, electrical, electro-optical, and catalytic properties.<sup>1-8</sup> Until now, many routes have been developed to fabricate such core-shell materials, such as the sol-gel process,<sup>1</sup> layer-by-layer technique,<sup>9</sup> template directed self-assembly,<sup>10</sup> and encapsulation of silica nanoparticles by in situ polymerization.<sup>11</sup>

The demand for high resolution and increased efficiency in phosphors for cathode ray tubes (CRTs) and field emissive displays has promoted the development of phosphors that perform at low voltages.<sup>12</sup> In particular, phosphors made up of small, ideally spherical particles are of interest because they offer the possibility of brighter cathodoluminescent performance, high definition, and much improved screen packing.<sup>13</sup> The ideal morphology of phosphor particles includes a perfect spherical shape, narrow size distribution (0.5–3  $\mu$ m), and nonagglomeration. Spherical morphology of the phosphors is good for high brightness and high resolution. Additionally, high packing densities and low scattering of light can also be obtained by using spherical phosphors. Nowadays, many synthetic routes have been developed to control the size and distribution of phosphor particles, such as spray pyrolysis<sup>14,15</sup> and fluxes precipitation.<sup>16</sup>

Silica can be easily made controllably in spherical morphology from nano- to micrometer size.<sup>17</sup> If the silica spheres are coated with layers of phosphors, a kind of core-shell phosphor materials with spherical morphology is obtained, and the size of the phosphor particles can be controlled by the silica cores. Furthermore, because silica is cheaper than most of the phosphor materials, the core-shell phosphor materials are cheaper than the pure phosphor materials in unit mass. Our group has been preparing various kinds of phosphor coatings on bulk silica glass and silicon wafer substrates via the sol-gel process.<sup>18,19</sup> It would be of great interest and importance to check if the core-shell phosphor materials can be prepared in a similar process.

It is well known that  $Mn^{2+}$ -doped zinc orthosilicate ( $\alpha$ -Zn<sub>2</sub>SiO<sub>4</sub>, willemite) has been widely used as a green component in plasma display panels (PDPs), CRTs, and electroluminescent devices due to its highly saturated color, strong luminescence, and long lifespan.<sup>20,21</sup> Recently, much attention has been paid to the synthesis and performance of nanostructural Zn<sub>2</sub>SiO<sub>4</sub>:Mn phosphors by solgel, hydrothermal, spray pyrolysis, and combustion methods, etc..<sup>22-26</sup> Interestingly, ZnO nanowires sheathed with Zn<sub>2</sub>SiO<sub>4</sub> were reported by Wang's group.<sup>27</sup> Herein, we select Zn<sub>2</sub>SiO<sub>4</sub>:Mn as the phosphor shells and silica spheres as the cores, respectively, to obtain the core-shell structured Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> materials via the sol-gel process and characterize the structure, morphology, and photoluminescent and cathodoluminescent properties of the resulting samples.

### Experimental

The starting materials for the preparation of  $Zn_2SiO_4$ :Mn@SiO<sub>2</sub> core-shell phosphors were tetraethoxysilane (TEOS)  $Si(OC_2H_5)_4$  (analytical reagent, AR), ammonium hydroxide NH<sub>4</sub>OH (AR), zinc acetate dihydrate  $Zn(OOCCH_3)_2$ ·2H<sub>2</sub>O (99.99%), manganese acetate tetrahydrate Mn(OOCCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (99.99%), citric acid monohydrate (AR), polyethylene glycol (PEG, molecular weight 10,000; AR), nitric acid HNO<sub>3</sub> (AR), ethanol C<sub>2</sub>H<sub>5</sub>OH (AR), and deionized water.

Preparation of monodisperse  $SiO_2$  spheres.—Monodisperse silica spheres were prepared by the Stöber method.<sup>17</sup> Typically, 25.7 mL TEOS was hydrolyzed in 171 mL ethanol in the presence of 196 mL ammonium hydroxide and 7.0 mL deionized water. The obtained silica spheres were centrifugally separated from the suspension and dried in an oven at 100°C for 24 h.

Surface coating of  $Zn_2SiO_4$ :Mn layer on  $SiO_2$  spheres.— The doping concentration of  $Mn^{2+}$  is 2 mol %, substituting for  $Zn^{2+}$  in  $Zn_2SiO_4$  layer, which has been optimized previously.<sup>20-25</sup> Stoichiometric weights of  $Zn(CH_3COO)_2 \cdot 2H_2O$  and  $Mn(CH_3COO)_2 \cdot 4H_2O$  were dissolved in 50 mL ethanol-water (8:1 in volume) solution in the presence of 1 mL nitric acid under stirring. Citric acid monohydrate as chelating agent (citric acid/metal

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ion = 2:1) and PEG as cross-linking agent were dissolved in the above solution, then silica spheres were added into the solution and the resulting mixture was further stirred for 3 h. The precipitates were filtered and dried at 100°C for 2 h, then preheated at 500°C for 3 h in a furnace with a heating rate of 60°C/h. The preheated samples were annealed to 1000°C at 100°C/h and held there for 3 h. In this way, the core-shell structured  $Zn_2SiO_4$ :Mn@SiO<sub>2</sub> materials have been obtained, and the whole process is shown in Scheme



Scheme 1. Formation process of Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> core-shell particles.

1. For multiple coating, the precursor solution is a little different from the above one because the surface of silica spheres were covered by  $Zn_2SiO_4$ :Mn layers which could not continue to react with  $Zn^{2+}$  and  $Mn^{2+}$ . Instead of citric acid and PEG, the stoichiometric weights of TEOS were added as silicon source in the mixing solution of  $Zn^{2+}$  and  $Mn^{2+}$ ; and then the solution was stirred for 2 days



**Figure 1.** XRD patterns for (a) the 1000°C-annealed SiO<sub>2</sub>, (b)  $Zn_2SiO_4:Mn@SiO_2$  core-shell particles, (c) pure  $Zn_2SiO_4:Mn$  powder sample, and (d) the JCPDS card (no. 37-1485) for  $Zn_2SiO_4$ . Miller indices of diffracting lattice planes are also shown.

before the silica spheres were added. The other processes were the same. The above process was repeated several times to increase the thickness of  $Zn_2SiO_4$ :Mn shells.

Characterizations .--- The X-ray diffraction (XRD) of the powder samples was examined on a Rigaku-Dmax-IIB using Cu Ka radiation ( $\lambda = 0.15405$  nm). Fourier transform infrared (FTIR) spectra were measured with Perkin-Elmer 580B infrared spectrophotometer with the KBr pellet technique. The morphology and composition of the samples were inspected using field emission scanning electron microscope (FE-SEM, XL30, Philips), transmission electron microscope (TEM, JEOL-2010, 200 kV), and energy-dispersive X-ray spectroscopy (EDS, JEOL JXA-840). The photoluminescence (PL) and the cathodoluminescence (CL) spectra were taken on a Hitachi F-4500 spectrofluorimeter equipped with a 150 W xenon lamp, 172 nm vacuum-uv (VUV) lamp (self-made) and 1-6 kV electron gun (self-made) as the excitation sources, respectively. The luminescence decay curves were obtained from a Lecroy Wave Runner 6100 digital oscilloscope (1 GHz) using 250 nm laser (pulse width = 4 ns, gate = 50 ns) as the excitation source (Continuum Sunlite OPO). All the measurements were performed at room temperature.

#### **Results and Discussion**

Formation and morphology of Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> core-shell particles.-XRD.-Figure 1 shows the XRD patterns for (a) the annealed SiO<sub>2</sub>, (b) Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub>, and (c) pure Zn<sub>2</sub>SiO<sub>4</sub>:Mn powder samples, as well as (d) the JCPDS card (no. 37-1485) for Zn<sub>2</sub>SiO<sub>4</sub> as a reference. For SiO<sub>2</sub> particles annealed at 1000°C (Fig. 1a), no diffraction peak is observed except for a broad band centered at  $2\theta = 22^{\circ}$ , which is the characteristic peak for amorphous SiO<sub>2</sub> (JCPDS 29-0085). For the Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> composite phosphors fired at 1000°C (Fig. 1b), besides the broad band at  $2\theta = 22^{\circ}$  from the amorphous SiO<sub>2</sub>, all the diffraction peaks belonging to crystalline willemite (a-Zn<sub>2</sub>SiO<sub>4</sub>, JCPDS card 37-1485) (Fig. 1d) are present, indicating that the coating layer of Zn<sub>2</sub>SiO<sub>4</sub>:Mn has crystallized well on the surface of silica spheres. This agrees well with the situation for the pure Zn<sub>2</sub>SiO<sub>4</sub>:Mn powder annealed at 1000°C (Fig. 1c, in which well-crystalline  $Zn_2SiO_4$  is observed). No other phase can be detected. Formation of the Zn<sub>2</sub>SiO<sub>4</sub>:Mn layer is due to the reaction of  $Zn^{2+}$ ,  $Mn^{2+}$  ions (on silica surfaces) with SiO<sub>2</sub> cores at high temperature (1000°C), as shown in Scheme 1. In the Pechini process, the citric acid first formed chelate complexes with Zn<sup>2+</sup> and Mn<sup>2+</sup>, then the left carboxylic acid groups in the citric acid reacted



Figure 2. FTIR spectra of (a) the as-formed SiO<sub>2</sub>, (b)  $1000^{\circ}$ C-annealed Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> core-shell sample, and (c) pure Zn<sub>2</sub>SiO<sub>4</sub>:Mn powder.

with PEG to form polyester with a suitable viscosity. The Zn<sup>2+</sup> and Mn<sup>2+</sup>, stabilized by the chelating and polymerizing process, were homogeneously distributed in the solution.<sup>28</sup> The Stöber process-derived silica particles contained a large amount of free hydroxyl groups (-OH) and silanol groups (Si–OH) on their surface (evidenced by FTIR spectra, see next section). By stirring silica particles in the solution, a lot of Zn<sup>2+</sup> and Mn<sup>2+</sup> were absorbed onto the silica particles by physical and chemical interactions. After the drying and annealing process, the Zn<sup>2+</sup> and Mn<sup>2+</sup> reacted with surface SiO<sub>2</sub> to form a Zn<sub>2</sub>SiO<sub>4</sub>:Mn layer on the silica cores.

FTIR.—The FTIR spectra of the as-formed SiO<sub>2</sub>, 1000°C fired Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> core-shell sample, and pure Zn<sub>2</sub>SiO<sub>4</sub>:Mn powder are shown in Fig. 2a-c, respectively. In Fig. 2a for the as-formed SiO<sub>2</sub> particles, the absorption bands and their corresponding vibrational models are 3432 cm<sup>-1</sup> ( $\nu_1$ , O–H), 1630 cm<sup>-1</sup> (O–H in H<sub>2</sub>O), 1102 cm<sup>-1</sup> ( $\nu_3$ , Si–O–Si), 952 cm<sup>-1</sup> ( $\nu_1$ , Si–OH), 802 cm<sup>-1</sup>  $(\nu_1, \text{Si-O-Si}), 474 \text{ cm}^{-1} (\nu_4, \text{Si-O}), \text{ where } \nu_1 \text{ is symmetric stretch-}$ ing,  $\nu_3$  is asymmetric stretching, and  $\nu_4$  is asymmetric deformation vibrations, respectively.<sup>29-32</sup> This indicates that the as-formed SiO<sub>2</sub> particles contain a large amount of OH groups and H<sub>2</sub>O on their surfaces. The surface Si-OH groups play an important role for bonding the metal ions from the coating sol and forming the Zn<sub>2</sub>SiO<sub>4</sub>:Mn layer on the SiO<sub>2</sub> surfaces in the following annealing process, as shown in Scheme 1. In Fig. 2b for the Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> coreshell sample, apart from the absorption peaks from silica cores (1125, 474 cm<sup>-1</sup>), the characteristic absorption peaks due to  $SiO_4$  $(v_1, 995, 894 \text{ cm}^{-1})$  and ZnO<sub>4</sub>  $(v_3, 577 \text{ cm}^{-1} \text{ from crystallized})$  $Zn_2SiO_4$  are present.<sup>33,34</sup> These absorption peaks are basically similar to those for the pure Zn<sub>2</sub>SiO<sub>4</sub>:Mn sample, as shown in Fig. 2c. This suggests that crystalline phase (Zn<sub>2</sub>SiO<sub>4</sub>) has formed after annealing at 1000°C, agreeing well with the results of XRD and further demonstrating the formation of crystalline Zn<sub>2</sub>SiO<sub>4</sub>:Mn coating layers on the silica surfaces via the sol-gel process and annealing treatment. Note that weak OH vibration can be found in Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> and Zn<sub>2</sub>SiO<sub>4</sub>:Mn samples due to the absorption of traces of water in the course of measurement.

*FESEM, EDS, TEM.*—Figure 3 shows the FE-SEM micrographs of (a) the as-formed SiO<sub>2</sub> particles, (b) the single  $Zn_2SiO_4$ :Mn layer coated SiO<sub>2</sub> core-shell ( $Zn_2SiO_4$ :Mn@SiO<sub>2</sub>) particles annealed at 1000°C, and (c) the EDS of  $Zn_2SiO_4$ :Mn@SiO<sub>2</sub> sample. From the FESEM micrograph of Fig. 3a we can observe that the as-formed SiO<sub>2</sub> particles are monodisperse spheres with smooth surfaces and nonaggregation, whose average size (in diameter) is about 750 nm.



Figure 3. FE-SEM micrographs of (a) the as-formed  $SiO_2$  particles, (b) the 1000°C-annealed core-shell  $Zn_2SiO_4:Mn@SiO_2$  particles, and (c) EDS of  $Zn_2SiO_4:Mn@SiO_2$  sample.

The core-shell  $Zn_2SiO_4:Mn@SiO_2$  particles (Fig. 3b) are also uniform spheres with a little aggregation, whose average size (diameter) seems larger than the pure SiO<sub>2</sub> particles due to the extra layers of  $Zn_2SiO_4:Mn$  on the SiO<sub>2</sub> spheres. However, it should be mentioned that the FE-SEM micrographs can only provide the basic information on the morphology of  $Zn_2SiO_4:Mn@SiO_2$  particles in large scale, and the core-shell structure of  $Zn_2SiO_4:Mn@SiO_2$  particles cannot be resolved from the FE-SEM micrographs. To further confirm the existence of  $Zn_2SiO_4:Mn@SiO_2$  particles, EDS was performed on the sample in Fig. 3b, as shown in



**Figure 4.** TEM micrographs for  $1000^{\circ}$ C-annealed (a) single and (b) double layer of Zn<sub>2</sub>SiO<sub>4</sub>:Mn-coated SiO<sub>2</sub> particles and (d) the bare SiO<sub>2</sub> particles as well as (c) the electron-diffraction pattern for (a).

Fig. 3c. Si, Zn, and O elements were detected on the surface of the complex particles. The Mn element was not detected clearly due to its low concentration (but it can be detected by the emission spectra, see next part). This provides additional evidence for the formation of coatings of crystalline  $Zn_2SiO_4$ :Mn on the SiO<sub>2</sub> particles.

In order to see the core-shell structure of Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> particles, TEM was performed. Representative TEM micrographs are shown for the SiO<sub>2</sub> particles coated by one and two layers of Zn<sub>2</sub>SiO<sub>4</sub>:Mn shell in Fig. 4a and b, respectively. In both cases, the core-shell structure for the Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> particles can be seen clearly due to the different electron penetrability for the cores and shells. The cores are black and the shells have gray color. The coreshell Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> particles remain spherical. The average thickness for a single-layer shell is about 150 nm (Fig. 4a), and that for a double-layer shell is about 220 nm (Fig. 4b). Obviously, the shell thickness increases with the increase of the number of coating times. As a comparison, no such kind of core-shell structure can be observed in bare SiO<sub>2</sub> particles, as shown in Fig. 4d. Fig. 4c shows the electron-diffraction pattern performed on the surface of the particles in Fig. 4a, which clearly demonstrates the formation of crystalline phase. Combined with the results of XRD in Fig. 1a, we can know that this crystalline phase must be Zn<sub>2</sub>SiO<sub>4</sub>:Mn. In summary, from the results of FE-SEM, EDS, and TEM, it can be concluded that Zn<sub>2</sub>SiO<sub>4</sub>:Mn layers have crystallized on the surface of SiO<sub>2</sub> spheres to form Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> core-shell particles, which mainly keep the original spherical morphology of the SiO<sub>2</sub> particles.

Luminescent and kinetic properties of  $Zn_2SiO_4$ :Mn@SiO\_2 coreshell particles.—Upon UV and VUV light excitation, the  $Zn_2SiO_4$ :Mn@SiO\_2 core-shell particles exhibit strong green luminescence. Figure 5 shows the (a) excitation and (b, c) emission spectra of the core-shell particles annealed at 1000°C, respectively.



Figure 5. (a) Excitation and (b, c) emission spectra of (single-layer)  $Zn_2SiO_4$ :Mn@SiO\_2 core-shell particles.

The excitation spectrum (Fig. 5a) contains an intense broad band with a maximum at 250 nm (5.0 eV) and a narrow shoulder at 223 nm (5.6 eV) extended to the VUV region (below 200 nm, not shown). The former corresponds to the charge-transfer band (CTB) of  $Mn^{2+}$  ion, and the latter originates from the absorption of the host lattice of  $Zn_2SiO_4$ . This indicates that an energy transfer occurs from the  $Zn_2SiO_4$  host lattice to  $Mn^{2+}$ .<sup>20-26</sup> Excitation into the CTB of  $Mn^{2+}$  at 250 nm or host band at 172 nm yields the emission spectrum with a maximum at 521–522 nm (Fig. 5b and c), which corresponds to the typical  ${}^{4}T_1({}^{4}G){}^{-6}A_1({}^{6}S)$  transition of  $Mn^{2+}$ . The green emitting can be explained when it is assumed that  $Mn^{2+}$  ions occupy a part of  $Zn^{2+}$  sites with four oxygen coordinated. The weak crystal field around  $Mn^{2+}$  results in the low splitting width of its 3d energy levels, and an emission at high energy (green) is observed. The mechanism involved in the green emission of  $Mn^{2+}$  in  $Zn_2SiO_4$  is shown in Fig. 6. Under excitation of 250 nm UV, an electron from



Figure 6. The PL mechanism for  $Mn^{2+}$  in  $Zn_2SiO_4$ .



**Figure 7.** The decay curve for the  ${}^{4}T_{1}({}^{4}G)-{}^{6}A_{1}({}^{6}S)$  (521 nm) emission of Mn<sup>2+</sup> in (single layer) Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> sample annealed at 1000°C.

the Mn<sup>2+</sup> ground state  ${}^{6}A_{1}({}^{6}S)$  is excited to the conduction band (CB) of Zn<sub>2</sub>SiO<sub>4</sub>. The process can be expressed as Mn<sup>2+</sup> +  $h\nu \rightarrow Mn^{3+}$  + e, where  $h\nu$  is the energy required in the photoexcitation of Mn<sup>2+</sup>. The free electrons in the CB can relax to the  ${}^{4}T_{1}({}^{4}G)$  excited states of Mn<sup>2+</sup> through a nonradiative process, then radiative transition from  ${}^{4}T_{1}({}^{4}G)$  excited state to the ground state  ${}^{6}A_{1}({}^{6}S)$  occurs, resulting in the green emission of Mn<sup>2+</sup> at 521 nm.<sup>35</sup>

In order to study the decay behavior of Mn<sup>2+</sup> luminescence in more detail in the Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> core-shell particles, the kinetic curve for the representative emission of Mn<sup>2+</sup>  ${}^{4}T_{1}({}^{4}G)-{}^{6}A_{1}({}^{6}S)$  (521 nm) was measured, as shown in Fig. 7. The decay curve can be well fitted into a double exponential function as  $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ , and the fitting results are shown inside Fig. 7. Two lifetimes, a fast one  $\tau_1 = 1.96$  ms and a slow one  $\tau_2 = 19.7$  ms have been obtained for the emission of Mn<sup>2+</sup>. The lattice of zinc silicate (Zn<sub>2</sub>SiO<sub>4</sub>) with willemite structure consists of corner-joined tetrahedral groups of  $[SiO_4]$  and  $[ZnO_4]$ . This structure contains two kinds of Zn<sup>2+</sup> sites, both having four nearestneighbor oxygens in a slightly distorted tetrahedral configuration. Accordingly, it can be assumed that the Mn<sup>2+</sup> ions occupy the two different  $Zn^{2+}$  sites in the crystalline layer of  $Zn_2SiO_4$  in the Zn<sub>2</sub>SiO<sub>4</sub>@SiO<sub>2</sub> core-shell particles, and the two different lifetimes arise from the  $Mn^{2+}$  ions occupied in the two different sites.<sup>30</sup> The average lifetime of  $Mn^{2+} {}^{4}T_{1}({}^{4}G) {}^{-6}A_{1}({}^{6}S)$  emission, defined as  $\langle \tau \rangle = (A_1 \tau_1^2 + A_2 \tau_2^2)/(A_1 \tau_1 + A_2 \tau_2)$ , can be determined to be  $(1) = (A_1)_1 + A_2 + 2P(A_1)_1 + A_2 + 2P(A_1$ ties of the electronic transitions within 3d<sup>5</sup> configuration of Mn<sup>2+</sup>

The PL intensity of  $Zn_2SiO_4:Mn@SiO_2$  core-shell particles can be tuned by the number of coatings. Figure 8 shows PL intensity as a function of the number of coatings. Clearly the PL intensity of  $Zn_2SiO_4:Mn@SiO_2$  core-shell particles increases with raising the coating number. Obviously this can be attributed to the increase of the thickness of  $Zn_2SiO_4:Mn$  shells on the  $SiO_2$  spheres. At present the PL intensity of three-layer  $Zn_2SiO_4:Mn@SiO_2$  particles is still not as strong as that of the pure  $Zn_2SiO_4:Mn$  sample, but this might be overcome by further coating and optimizing other experimental conditions such as annealing temperature and time as well as the doping concentration of  $Mn^{2+}$ , which are underway.

The Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> core-shell particles also show a strong green emission under low-voltage cathode ray excitation, and the resulted CL spectra are identical with those of the PL emission spectra shown in Fig. 5b and c due to the  ${}^{4}T_{1}({}^{4}G){}^{-6}A_{1}({}^{6}S)$  transition of Mn<sup>2+</sup>. The CL emission intensity for one-layer Zn<sub>2</sub>SiO<sub>4</sub>:Mn-coated SiO<sub>2</sub> particles has been investigated as a function of filament current



**Figure 8.** The PL emission intensity of  $Mn^{2+}$  in  $Zn_2SiO_4:Mn@SiO_2$  sample as a function of the coating number (*N*): (a) N = 1, (b) N = 2, and (c) N = 3.

and accelerating voltage, as shown in Fig. 9a and b, respectively. Under 4 kV electron-beam excitation, the CL intensity increases with increasing the filament current from 14 to 18 mA (Fig. 9a). Similarly, when the filament current is fixed at 14 mA, the CL intensity also increases with raising the accelerating voltage from 1 to 6 kV (Fig. 9b).



Figure 9. The CL emission intensity of  $Mn^{2+}$  as a function of (a) filament current and (b) accelerating voltage.

#### Conclusions

Spherical core-shell structured Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> particles with uniform size distribution have been successfully prepared by the sol-gel method followed by annealing at high temperature. Upon UV, VUV, and cathode ray excitation, the luminescence properties of the Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> core-shell particles are typical of those of Zn<sub>2</sub>SiO<sub>4</sub>:Mn, i.e., green band emission at 521 nm due to  ${}^{4}T_{1}({}^{4}G)-{}^{6}A_{1}({}^{6}S)$  transition of Mn<sup>2+</sup>. The PL intensity of the coreshell particles can be tuned by the number of coatings. With the increase of the number of coatings, the PL intensity increases. The CL intensity of the Zn<sub>2</sub>SiO<sub>4</sub>:Mn@SiO<sub>2</sub> particles increases with raising the filament current and cathode voltage. The advantages of the phosphors prepared by this process are the easy availability of homogeneous spherical morphology in different size, and its wide practicality for other phosphor materials.

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#### References

- 1. R. A. Caruso and M. Antonietti, Chem. Mater., 13, 3272 (2001). 2. F. Caruso, M. Spasova, and V. Salgueirno-Maceria, Adv. Mater. (Weinheim, Ger.), 13. 1090 (2001).
- 3. H. Giesche and E. Matijevic, J. Mater. Res., 9, 436 (1994).
- 4. H. Sertchook and D. Avnir, Chem. Mater., 15, 1690 (2003).
- 5. M. Giersig, T. Ung, L. M. Liz-Marzan, and P. Mulvaney, Adv. Mater. (Weinheim,

Ger.), 9, 570 (1997).

- M. Ocana, W. P. Hsu, and E. Matijevic, Langmuir, 7, 2911 (1991).
- W. P. Hsu, R. C. Yu, and E. Matijevic, J. Colloid Interface Sci., 156, 56 (1993).
   M. S. Fleming, T. K. Mandal, and D. R. Walt, Chem. Mater., 13, 2210 (2001).
- 9. P. Schuetzand and F. Caruso, Chem. Mater., 14, 4509 (2002).
- 10. S. R. Hall, S. A. Davis, and S. Mann, Langmuir, 16, 1454 (2000).
- 11. I. Sondi, T. H. Fedynyshyn, R. Sinta, and E. Matijevic, Langmuir, 16, 9031 (2000). 12. M. I. Martinez-Rubio, T. G. Ireland, G. R. Fern, J. Silver, and M. J. Snowden,
- Langmuir, 17, 7145 (2001).
  13. A. Vecht, C. Gibbons, D. Davies, X. Jing, P. Marsh, T. G. Ireland, J. Silver, and A. Newport, J. Vac. Sci. Technol. B, 17, 750 (1999).
- 14. K. Y. Jung, D. Y. Lee, Y. C. Kang, and H. D. Park, J. Lumin., 105, 127 (2003)
- 15. Y. C. Kang, I. W. Lenggoro, S. B. Park, and K. Okuyama, Mater. Res. Bull., 35, 789 (2000).
- 16. A. Celikkaya and M. Akinc, J. Am. Ceram. Soc., 73, 2360 (1990).
- 17. W. Stöber, A. Fink, and E. Bohn, J. Colloid Interface Sci., 26, 62 (1968).
- M. Yu, J. Lin, J. Fu, H. J. Zhang, and Y. C. Han, J. Mater. Sci., 13, 1413 (2003). 19. M. Yu, J. Lin, Z. Wang, J. Fu, S. Wang, H. J. Zhang, and Y. C. Han, Chem. Mater., 14, 2224 (2002).
- 20. G. Blasse, and B. C. Grabmaier, Luminescent Materials, Springer-Verlag, Berlin, Heidelberg (1994).
- 21. X. Ouyang, A. H. Kitai, and T. Xiao, J. Appl. Phys., 79, 3229 (1996).
- T. S. Copeland, B. I. Lee, J. Qi, and A. K. Elrod, J. Lumin., 97, 168 (2002).
   T. S. Ahmadi, M. Haase and H. Weller, *Mater. Res. Bull.*, 35, 1869 (2000).
   Y. C. Kang and S. B. Park, *Mater. Res. Bull.*, 35, 1143 (2000).
- 25. A. Roy, S. Polarz, S. Rabe, B. Rellinghaus, H. Zähres, F. E. Kruis, and M. Driess, Chem.-Eur. J., 10, 1565 (2004). 26.
- R. P. Sreekanth Chakradhar, B. M. Nagabhushana, G. T. Chandrappa, K. P. Ramesh, and J. L. Rao, J. Chem. Phys., 121, 10250 (2004).
- 27. X. Wang, C. J. Summers, and Z. L. Wang, Adv. Mater. (Weinheim, Ger.), 16, 1215 (2004).
- 28 M. Kakihana and K. Domen, MRS Bull., 25(9), 27 (2000).
- 29 A. Kioul and L. Mascia, J. Non-Cryst. Solids, 175, 169 (1994)
- 30. S. Kook Mah and I. J. Chung, J. Non-Cryst. Solids, 183, 252 (1995).
- Y. Chen and J. O. Iroh, Chem. Mater., 11, 1218 (1999). 31
- 32. J. Méndez-Vivar and A. Mendoza-Bandala, J. Non-Cryst. Solids, 261, 127 (2000).
- C. C. Lin and P. Y. Shen, J. Non-Cryst. Solids, 171, 281 (1994). 33. 34
- A. M. Pires and M. R. Davolos, Chem. Mater., 13, 21 (2001).
- R. Selomulya, S. Ski, and K. Pita, *Mater. Sci. Eng.*, *B*, 100, 136 (2003).
   A. Patra, G. A. Baker, and S. N. Baker, *J. Lumin.*, 111, 105 (2005).
- 37. S. Murakami, M. Herren, D. Rau, and M. Morita, Inorg. Chim. Acta, 300-302, 1014 (2000).