Direct white-light from core-shell-like sphere with $Sr_3MgSi_2O_8$: Eu^{2+}, Mn^{2+} coated on Sr_2SiO_4:Eu^{2+}*

LI Jian (李建)[1,2], **DENG Jia-chun** (邓家春)[2]**, **LU Qi-fei** (陆启飞)[3], and **WANG Da-jian** (王达健)[1,3]**

1. Key Lab. of Display Materials & Photoelectronic Devices, Ministry of Education, Tianjin University of Technology, Tianjin 300384, China

2. School of Science, Tianjin University of Technology, Tianjin 300384, China

3. Institute of Materials Physics, Tianjin University of Technology, Tianjin 300384, China

A method of color mixture for white light is presented with $Sr_3MgSi_2O_8$:Eu^{2+}, Mn^{2+} shell coated on Sr_2SiO_4:Eu^{2+} core by spray pyrolysis procedure. Upon near ultraviolet (NUV) excitation, a 550 nm band emission of Eu^{2+} from core host combines with the simultaneous emissions of Eu^{2+} at 457 nm and Mn^{2+} at 683 nm based on energy transfer in the shell lattice to generate warm white light with color rendering index (CRI) of 91. With such a core-shell-like structure, the re-absorption of blue light from shell layer can be effectively suppressed, and the chemical stability of the phosphor is verified experimentally to be superior to that of the Sr_2SiO_4:Eu^{2+}. This new proposed phosphor provides great potential in the color mixture of blending-free phosphor converted white NUV light emitting diode (LED) devices.

Solid state lighting of white-light-emitting diode (WLED) technology has ever emerged into the next-generation lighting source[1-3]. The currently commercialized WLEDs are fabricated by combining yellow-emitting phosphor of $Y_3Al_5O_{12}$:Ce^{3+} with blue-emitting phosphor of InGaN. For indoor lighting, this combination is not satisfactory to construct full spectrum white light[4-6] owing to the deficits of green component and red component in color mixture. An approach by combining AlGaInP red chips with InGaN blue chips indeed results in the problems of unmatched forward bias driving current, which leads to a time-dependent shift of the color point. A more reasonable solution[7,8] has been proposed by combining tricolor phosphors of blue, green and red with near ultraviolet (NUV) chips. It has been recognized that the NUV chips with 380 nm to 410 nm emission exhibit the highest internal quantum efficiencies[9,10]. Many NUV excitable phosphors have emerged recently[11-13], such as $SrZn_2(PO_4)_2$:Eu^{2+}, Mn^{2+} and $Ca_3Sc_2Si_3O_{12}$:Ce^{3+}, Mn^{2+}. The approach by using Mn^{2+} for red component is comparable to all-nitride phosphor in effective cost[14]. It is noted that the color mixture for white light with these phosphors is realized by blending the micrometer sized powder, which leads to re-absorption among particles. A novel method by using core-shell structured phosphor[15-17] has been proposed to suppress the re-absorption. For the presently concerned $Ba_3MgSi_2O_8$ and Sr_2SiO_4 silicate hosted phosphors, their high quantum efficiencies have drawn the attention of re-

searchers[18,19]. We also have been involved in a series of approaches[14,20,21] with respect to a simultaneous band emission of red and blue light and a full spectrum white emission. The superior chemical stability of $A_3MgSi_2O_8$ (A=Ba, Sr, Ca) to A_2SiO_4 (A=Ba, Sr, Ca) has been examined elsewhere[22], and the thermal stablity of Sr_2SiO_4:Eu^{2+} can be solved efficiently by remote phosphor technology[23]. Thus, a suitable combination of host with green emitting and red emission of Mn ion will be expected to generate the desired white light without phosphor blending or re-absorption of emission among particles.

In this paper, we report a white light emitting phosphor obtained by coating $Sr_{2.97}Mg_{0.9}Si_2O_8$:$0.03Eu^{2+}$, $0.1Mn^{2+}$ with 457 nm blue and 683 nm red band emissions on $Sr_{1.97}SiO_4$:$0.03Eu^{2+}$ with 550 nm yellow band emission. This core-shell structured phosphor has a strong excitation band in the wavelength range of 310–430 nm, which matches well with NUV chip.

The phosphor in an optimized composition of $Sr_{1.97}SiO_4$:$0.03Eu^{2+}$ was obtained by spray pyrolysis procedure in this paper. A composite sol in a stoichiometric $Sr_{2.97}Mg_{0.9}Si_2O_8$:$0.03Eu^{2+}$, $0.1Mn^{2+}$ was prepared by using tetraethyl orthosilicate (TEOS), magnesium nitrate hexhydrate ($Mg(NO_3)_2 \cdot 6H_2O$), $Eu(NO_3)_3 \cdot 6H_2O$, $C_4H_6MnO_4 \cdot 4H_2O$ and barium nitrate ($Sr(NO_3)_2$) as precursors. Pre-synthesized $Sr_{1.97}SiO_4$:$0.03Eu^{2+}$ particles were mixed with above-mentioned sol solution with different mole ratios of $Sr_{1.97}SiO_4$:$0.03Eu^{2+}$: $Ba_{2.97}Mg_{0.9}Si_2O_8$:$0.03Eu^{2+}$, $0.1Mn^{2+}$ from 3 to 1/3, and

designated as sample 1 for 3:1, sample 2 for 2:1, sample 3 for 1:1, sample 4 for 1:2 and sample 5 for 1:3, respectively. The as-mixed slurry was subjected to spray in an atomizer (LabPlant, UK) with a heated air flow at 120 $^{\circ}$C. Then as-sprayed xerogel particles were fired in an electrical box furnace at 1300 $^{\circ}$C for 3 h in a reducing atmosphere of H_2 (8%) and N_2 (92%) to produce the desired core-shell phosphor samples.

The X-ray diffraction (XRD) patterns of as-received phosphors were recorded with a diffractometer (Rigaku D/max-2500/pc, $\lambda_{\text{Cu-K}\alpha}$=1.54062 nm, Japan). The color coordinate, correlated color temperature (CCT) and color rendering index (CRI) were measured with a fluorescence spectrometer equipped with a 350 nm Xe flash lamp (EX-1000, Everfine Co. Ltd., China). Photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra of samples were recorded by a fluorescence spectrometer equipped with a 350 nm Xe flash lamp (Hitachi F-4600, Japan), and the excitation and emission slits were both set to be 2.5 nm. All measurements were carried out at room temperature.

Fig.1 shows the schematic diagram of core-shell structure and its resultant color mixture for warm white. The as-sprayed particles on the surface of $Sr_{1.97}SiO_4$:0.03Eu^{2+} form the crystalline phase of $Sr_{2.97}Mg_{0.9}Si_2O_8$:0.03Eu^{2+}, 0.1Mn^{2+} at high temperature. With increasing the ratio of $Sr_{2.97}Mg_{0.9}Si_2O_8$:0.03Eu^{2+}, 0.1Mn^{2+} to $Sr_{1.97}SiO_4$:0.03Eu^{2+}, the coating tends to be thicker, leading to a higher emitting intensity of $Sr_{2.97}Mg_{0.9}Si_2O_8$:0.03Eu^{2+}, 0.1Mn^{2+}.

Fig.2 shows the XRD patterns of as-prepared samples 1−5. All the samples are identified to be the mixture of $Sr_3MgSi_2O_8$ phase and Sr_2SiO_4 phase. The diffraction peaks marked by square can be well indexed to a monoclinic-type structure of $Sr_3MgSi_2O_8$ with JCPDS card No.10-0075, while that marked by inverted triangle can be well indexed to an orthorhombic-type structure of Sr_2SiO_4 with JCPDS card No.39-1256. From sample 1 to 5, the diffraction intensity of Sr_2SiO_4 phase decreases gradually. Other impurity phases are not detected from the XRD patterns, indicating independent formation of $Sr_3MgSi_2O_8$ host phase without reaction of constitutes in the as-sprayed xerogel.
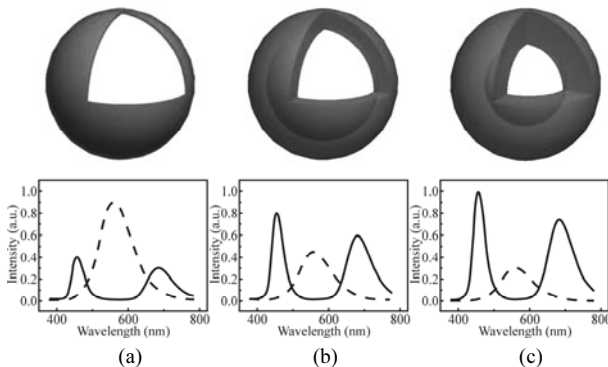

Fig.1 Schematic diagrams of core-shell-like structure models and tri-color emission spectra of as-prepared (a) sample 1, (b) sample 3 and (c) sample 5
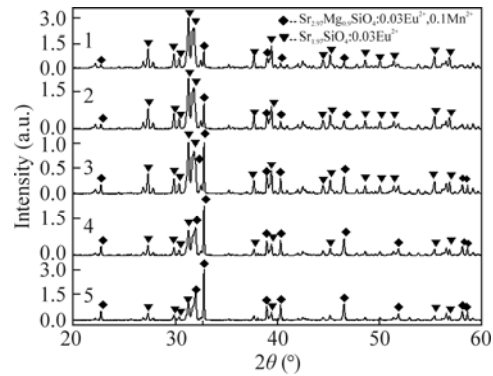
Fig.2 XRD patterns of samples 1−5 with varied mole ratio of $Sr_{1.97}SiO_4$:0.03Eu^{2+} to $Sr_{2.97}Mg_{0.9}Si_2O_8$:0.03Eu^{2+}, 0.1Mn^{2+}

Fig.3 shows the transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) analyses for $Sr_{1.97}SiO_4$:0.03Eu^{2+} and $Sr_{1.97}SiO_4$:0.03Eu^{2+}-$Sr_{2.97}Mg_{0.9}Si_2O_8$:0.03Eu^{2+}, 0.1Mn^{2+} phase-coexisting phosphor of sample 3. Single phase Sr_2SiO_4 through spraying appears as a coated sphere with distinct edges. The EDS element analysis verifies the existence of Sr, Si, O and Eu which should be included in $Sr_{1.94}SiO_4$:0.06Eu^{2+}, even though there are some differences between the detected and nominal compositions in quantity. For the Sr_2SiO_4-$Sr_3MgSi_2O_8$ coexisting sample, we observe that the cage-like structure remains unchanged. However, lots of fragments are observed to adhere to the frame of cage-like structure. The EDS element analysis for the Sr_2SiO_4-$Sr_3MgSi_2O_8$ coexisting sample verifies the existence of Sr, Si, O, Eu, Mg and Mn. Considering the information from the XRD results, we propose that these fragments are assigned to the $Sr_3MgSi_2O_8$.
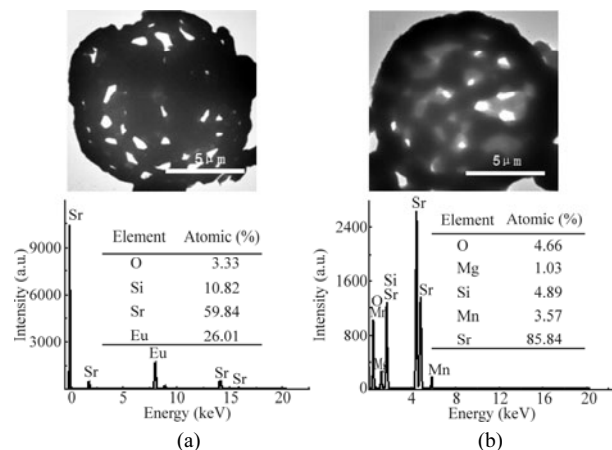

Fig.3 TEM and EDS analyses for (a) $Sr_{1.97}SiO_4$:0.03Eu^{2+} single-phase phosphor sample and (b) $Sr_{1.94}SiO_4$:Eu^{2+} -$Sr_{2.97}Mg_{0.9}Si_2O_8$:0.03Eu^{2+}, 0.1Mn^{2+} phase-coexisting phosphor of sample 3

Fig.4 shows the PLE and PL spectra of $Sr_{2.97}Mg_{0.9}Si_2O_8$:0.03Eu^{2+}, 0.1Mn^{2+} and the $Sr_{1.97}SiO_4$:0.03Eu^{2+} phosphors, respectively. The Eu^{2+} excitation band of $Sr_{2.97}Mg_{0.9}Si_2O_8$:

$0.03Eu^{2+}$, $0.1Mn^{2+}$ can be fitted into three Gaussian components with peaks at 280 nm, 345 nm and 390 nm, corresponding to the $^8S_{7/2} \to {}^2t_{2g}$ (281 nm, 343 nm) and $^8S_{7/2} \to {}^2e_g$ (391 nm) electronic transition absorption of the Eu^{2+}, respectively[19]. Compared with the excitation of Eu^{2+}, the Mn^{2+} excitation intensity is very weak for the 3d-3d forbidden transition[14,21]. Both $Sr_{2.97}Mg_{0.9}Si_2O_8$: $0.03Eu^{2+}$, $0.1Mn^{2+}$ and the $Sr_{1.97}SiO_4:0.03Eu^{2+}$ show a broad absorption in the NUV region.

The blue emission band at 457 nm is attributed to 5d-4f electron transition of Eu^{2+}, while the red band at 683 nm is attributed to the transition of Mn^{2+} through an effective energy transfer from Eu^{2+} for $Sr_{2.97}Mg_{0.9}Si_2O_8$: $0.03Eu^{2+}$, $0.1Mn^{2+}$[14]. The photoluminescence spectrum of $Sr_{1.97}SiO_4:0.03Eu^{2+}$ shows a 550 nm broad and asymmetric emission band with a full width at half maximum (FWHM) of 110 nm.
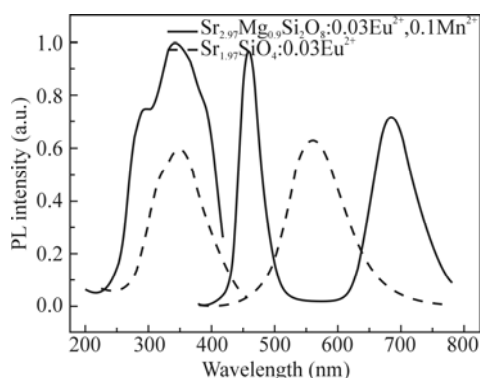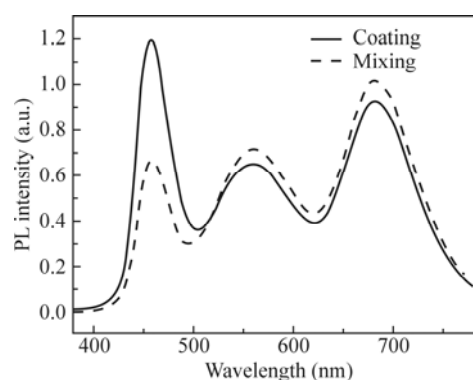
Fig.4 PLE and PL spectra of $Sr_{2.97}Mg_{0.9}Si_2O_8:0.03Eu^{2+}$, $0.1Mn^{2+}$ phosphor and $Sr_{1.97}SiO_4:0.03Eu^{2+}$ phosphor

Fig.5 depicts the PL spectra of samples 1−5. It is observed that the emission spectra show three emission bands at 457 nm, 550 nm and 683 nm. The simultaneous band emissions at both 457 nm and 683 nm originate from $Sr_{2.97}Mg_{0.9}Si_2O_8:0.03Eu^{2+}$, $0.1Mn^{2+}$, while the 550 nm emission originates from $Sr_{1.97}SiO_4:0.03Eu^{2+}$. The emission intensities of 435 nm and 623 nm are both gradually enhanced from sample 1 to sample 5, while the 550 nm emission of $Sr_{1.97}SiO_4:0.03Eu^{2+}$ is gradually decreased, which is consistent with the XRD results.
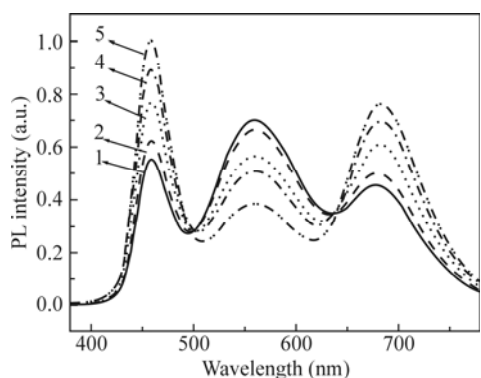
Fig.5 PL spectra of samples 1−5 with varied mole ratio of $Sr_{1.97}SiO_4:0.03Eu^{2+}$ and $Sr_{2.97}Mg_{0.9}Si_2O_8:0.03Eu^{2+}$, $0.1Mn^{2+}$

Fig.6 depicts a comparison of PL spectra of core-shell-like and mixed phosphors with $Sr_{2.97}Mg_{0.9}Si_2O_8:0.03Eu^{2+}$, $0.1Mn^{2+}$ and $Sr_{1.97}SiO_4:0.03Eu^{2+}$. The PL spectra of core-shell phosphors and mixture phosphors both cover the visible spectrum area. However, there is an obvious difference about the intensity of blue light in the range of 400–500 nm. For the mixed phosphors, the blue light is re-absorbed by $Sr_{1.97}SiO_4:0.03Eu^{2+}$, while the phosphor by coating $Sr_{2.97}Mg_{0.9}Si_2O_8:0.03Eu^{2+}$, $0.1Mn^{2+}$ on $Sr_{1.97}SiO_4:0.03Eu^{2+}$ phosphor decreases the re-absorption of blue light efficiently. The blue light of $Sr_{2.97}Mg_{0.9}Si_2O_8:0.03Eu^{2+}$, $0.1Mn^{2+}$ phosphor is observed not to be reabsorbed by $Sr_{1.97}SiO_4: 0.03Eu^{2+}$ phosphor directly owing to its location at the center of core-shell structure.

Fig.6 A comparison of PL spectra between core-shell-like and mixed phosphors with $Sr_{2.97}Mg_{0.9}Si_2O_8:0.03Eu^{2+}$, $0.1Mn^{2+}$ and $Sr_{1.97}SiO_4:0.03Eu^{2+}$

As shown in Fig.7, we test the chemical stability of core-shell-like phosphor with $Sr_{2.97}Mg_{0.9}Si_2O_8:0.03Eu^{2+}$, $0.1Mn^{2+}$ and $Sr_{1.97}SiO_4:0.03Eu^{2+}$ by using 20% diluted hydrochloric acid solution. Assume the original PL intensity to be 100%, and divide every sample into seven parts. The samples were immerged into diluted hydrochloric acid solution, then the PL intensity was tested by taking out of samples, and the samples were dried every hour using the same method. It is observed that the chemical stability of core-shell-like phosphor is superior to that of independent $Sr_{1.97}SiO_4:0.03Eu^{2+}$. With the protection of shell-layer of $Sr_{2.97}Mg_{0.9}Si_2O_8:0.03Eu^{2+}$, $0.1Mn^{2+}$, the chemical stability of core-shell-like phosphor is enhanced to about 89%.
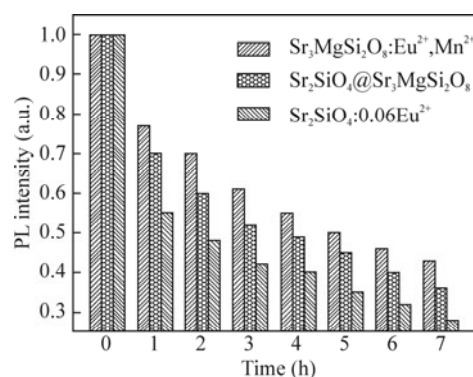
Fig.7 PL intensities of different phosphors versus the immerging duration of phosphor in diluted hydrochloric acid solution

Fig.8 traces the Commission International de l'Eclairage (CIE) chromaticity coordinates, and shows the photographs of samples 1 to 5. From sample 1 to sample 5, the CIE chromaticity coordinates move from a reddish white region (x=0.2436, y=0.1525) to a yellow region (x=0.3901, y=0.4201). The CIE chromaticity coordinates for sample 3 (x=0.3336, y=0.3025) show a high CRI of 91 with the CCT of 5275 K, indicating the potential application in WLEDs and display devices.
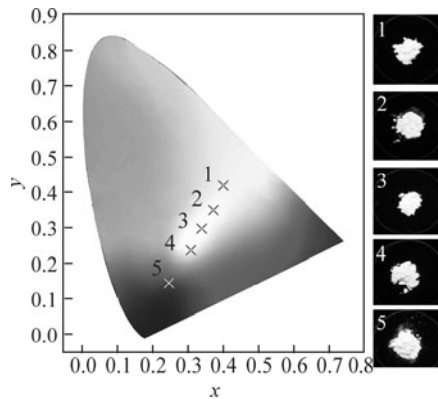
Fig.8 CIE chromaticity coordinates and photographs of the illuminated samples

We construct a core-shell-like phosphor in a form of $Sr_{2.97}Mg_{0.9}Si_2O_8$:0.03Eu^{2+}, 0.1Mn^{2+} coated on $Sr_{1.97}SiO_4$:0.03Eu^{2+}. A tri-color combination of 457 nm blue, 683 nm red and 550 nm yellow band emissions generates the white light. Compared with the conventional directly mixing phosphor operation, this strategy shows obvious advantage to suppress the re-absorption of blue light by blue-excitable phosphor particle in multi-component phosphor mixture. The shell layer of $Sr_{2.97}Mg_{0.9}Si_2O_8$:0.03Eu^{2+}, 0.1Mn^{2+} on the $Sr_{1.97}SiO_4$:0.03Eu^{2+} core exhibits the increased stability in acid solution immersion tests, providing an effective option to solve stability issues for yellow emitting $Sr_{1.97}SiO_4$: 0.06Eu^{2+} phosphor. The $Sr_{1.97}SiO_4$: 0.06Eu^{2+} coated $Sr_{2.94}Mg_{0.9}Si_2O_8$:0.06Eu^{2+}, 0.1Mn^{2+} phosphor used for WLEDs with high CRI of 91 is obtained. The construction for the desired color quality prior to device packaging will simplify the conventional blending operation of micrometer-sized phosphor particles, providing great potential in NUV WLEDs.

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