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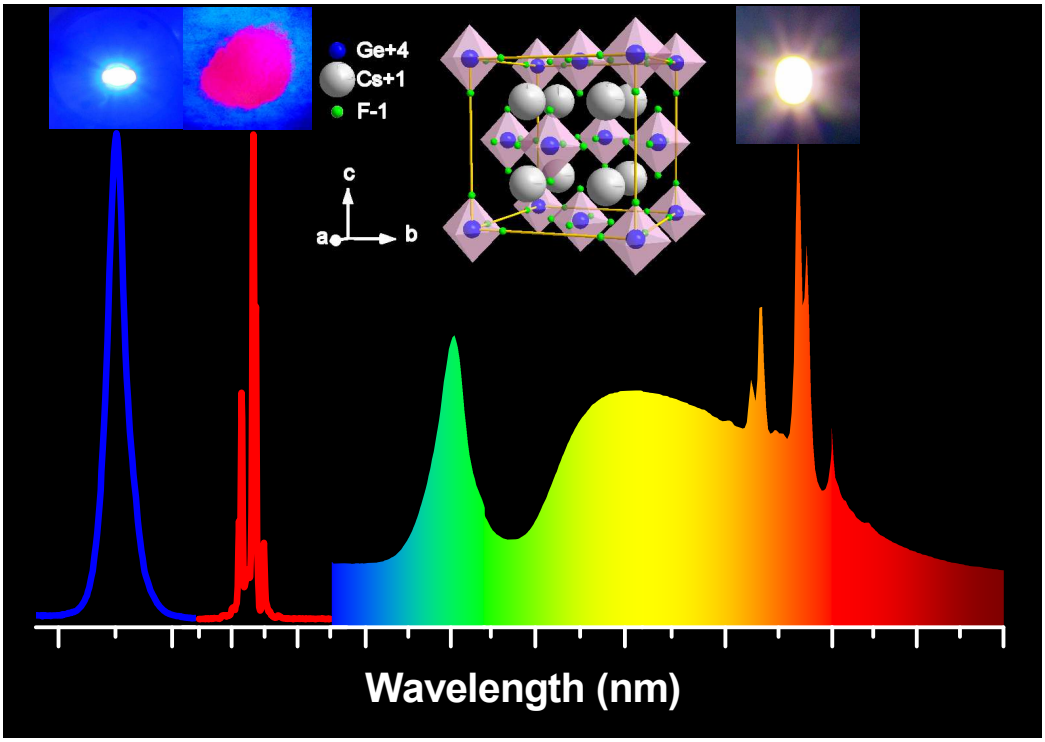
Graphical Abstract

Red phosphor $Cs_2GeF_6:Mn^{4+}$ synthesized by the cation exchange method exhibits intense red emission with high colour-purity. Warm WLED fabricated with this phosphor emits intense white light under 20 mA current excitation.



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Highly efficient red phosphor $Cs_2GeF_6:Mn^{4+}$ for warm white light-emitting diodes

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Red phosphor $Cs_2GeF_6:Mn^{4+}$ has been synthesized by the cation exchange method. The as-prepared phosphor was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometer (EDS), atomic absorption spectrophotometer (AAS), thermogravimetry (TG) and differential scanning calorimetry (DSC). Its optical properties were investigated by photo-luminescent spectra (PL), diffuse reflectance spectra (DRS), low-temperature emission spectrum and the luminescence decay curve. The sample doped with 8.78 mol% Mn^{4+} exhibits intense red emission with high thermal stability and appropriate CIE coordinates (x = 0.69, y = 0.31), and its emission intensity is higher than that of commercial $K_2TiF_6:Mn^{4+}$. The white light-emitting diodes (WLEDs) fabricated with this sample exhibits intense warm white-light with low color temperature (T_c = 3673 K), high color rendering index (R_a = 84.9) and high luminous efficacy (LE = 141.5 lm/W). So $Cs_2GeF_6:Mn^{4+}$ may be a promising red component for warm WLEDs.

Introduction

White light-emitting diodes (WLED) have been extensively used in recent illumination systems, due to their high efficiency, long lifetime, energy-saving and environmental friendly properties.[1-3] However, the commercial WLEDs fabricated GaN-based LED with $YAG:Ce^{3+}$ (YAG) have low colour rendering index (R_a) and high colour temperature (T_c), because of the absence of red components in their spectra.[4-6] To obtain warm WLEDs, some red phosphors were introduced during the fabrication of YAG-type WLEDs.[7,8]

Recently, Mn^{4+} doped alkaline hexafluorides, $A_2XF_6:Mn^{4+}$ (A = K, Na and Cs, X = Si, Ge, Zr and Ti), have received a great of interests, since these phosphors show intense red emission with broad excitation band in the blue region. And they could find potential application in warm WLEDs.[9-18] As it known to all, Mn^{4+} is sensitive to surrounding environment and hard to be controlled. Hence, Mn^{4+} doped fluoride complexes were prepared by different methods, such as the cation exchange method,[9] the co-precipitation method,[10] and the wet chemical etching route,[18]. For example, in our previous work,[19] we have synthesized $Na_2XF_6:Mn^{4+}$ (X = Si, Ge, Ti) red phosphors by the co-precipitation method. Cs_2GeF_6 also belongs to the family of alkaline hexafluorides with cubic structure.[20] Mn^{4+} doped Cs_2GeF_6 has been synthesized by chemically etching Ge shots in aqueous $HF/CsMnO_4$ solutions.[18] However, this wet chemical etching route to prepare $Cs_2GeF_6:Mn^{4+}$ has some drawbacks, such as expensive cost of Ge shots, long reaction time and low yield.

In this article, red phosphor $Cs_2GeF_6:Mn^{4+}$ was prepared *via* the cation exchange method with K_2MnF_6 as Mn^{4+} source. The optical properties of this phosphor were investigated in details. The as-prepared $Cs_2GeF_6:Mn^{4+}$ shows intense red emission with high colour-purity under blue light excitation. The optical performance of WLEDs can be improved by introducing red phosphor $Cs_2GeF_6:Mn^{4+}$.

Experimental

Synthesis

All source materials in this work, including HF (40 *wt*%), CsF, $KMnO_4$, GeO_2, H_2O_2 (30 *wt*%) and KHF_2 were of analytical grade and without any purification. Commercial YAG yellow phosphor was purchased from Shenzhen Quanjing Photon Co. Ltd., China. Commercial $K_2TiF_6:Mn^{4+}$ red phosphor was purchased from Intematix Corporation. K_2MnF_6 was synthesized according to the reference.[21] Specifically, 0.40 mol KHF_2 and 10 mmol $KMnO_4$ were dissolved in HF (40 *wt*%) solution, then 10 ml H_2O_2 (30 *wt*%) was added to precipitate K_2MnF_6 yellow powders with 30 min magnetically stirring. Thereafter, the above mixture was cooled in an ice bath for 30 min and then filtered. The resulting K_2MnF_6 solid product was collected carefully from the cup, washed extensively with methanol several times, and dried at 80 ^oC for 12 hours.

$Cs_2GeF_6:Mn^{4+}$ was prepared by the cation exchange method with as-prepared K_2MnF_6. In a typical synthesis, 5 mmol GeO_2 was added into 10 ml HF (40 *wt*%) solution until completely dissolved. Then 0.5 mmol K_2MnF_6 and 11 mmol CsF were put into the colorless transparent solution in order. After 30 min magnetically stirring and a quick cooling process in salt-ice bath, the precipitates were collected, washed with methanol several times and dried at 80 ^oC. At last, the $Cs_2GeF_6:Mn^{4+}$ red phosphor sample was obtained.

Fabrication of LED devices.

The single red LED was fabricated by combing GaN chips (~ 450 nm) with the mixture of red phosphors $Cs_2GeF_6:Mn^{4+}$ and

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Electronic Supplementary Information (ESI) available: [details of the relative concentration, concentration dependence of the relative emission intensity of Mn^{4+} in $Cs_2GeF_6:Mn^{4+}$ and decay curve]. See DOI: 10.1039/x0xx00000x

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epoxy resin. Firstly, the phosphors were mixed with epoxy resin thoroughly and coated on the surface of the GaN chip. Then the device was packaged with epoxy resin and solidified at 150 ^{o}C for 1 h. At last red LED was obtained. Similarly, WLEDs were fabricated by coating the mixture of commercial YAG, epoxy resin and $Cs_2GeF_6:Mn^{4+}$ (the ratio of mass is 1:10: *m*, *m* = 0, 0.5, 1, 1.5 and 2) on GaN chips.

Characterizations

The crystal structure of the as-prepared product was investigated on a powder X-ray diffraction (XRD) with an X-ray diffractometer using Cu Kα radiation (λ = 0.15406 nm) and a graphite monochromator from 15° to 70°. The corresponding surface morphology and structure were observed by a scanning electron microscopy (SEM, FEI Quanta 200 Thermal FE Environment scanning electron microscopy) with an attached energy-dispersive X-ray spectrometer (EDS). Compositional analysis was performed on a Shimadzu AA-6300 atomic absorption spectrophotometer (AAS). The diffuse reflectance ultraviolet-visible spectra (DRS) and decay curve were collected on an Cary 5000 UV-Vis-NIR spectrophotometer and an Edinburgh FLS920 combined fluorescence lifetime and steady state spectrometer with a 450 W Xe lamp and 60 W μF flash lamp, respectively. Excitation and emission spectra were examined on a Cary Eclipse FL1011M003 (Varian) spectrofluorometer with the excitation and emission slits 2.5, and the xenon lamp was used as excitation source. The low temperature emission spectrum (12 K) was measured by using an Xe lamp connected with a monochromator as source. And the sample temperature was controlled by a temperature controller (YANGMING XMTG-6311). The electro-luminescent (EL) spectra of WLEDs were recorded on a high accurate array spectrometer (HSP6000).

Results and discussion

Structure and morphology

Fig. 1 is the XRD pattern of as-prepared $Cs_2GeF_6:Mn^{4+}$, which is consistent with the corresponding JCPDS card of Cs_2GeF_6 (No. 76-1398). This result indicates that the obtained phosphor shares the single phase with the cubic structure (space group of *Fm-3m*, *a* = *b* = *c* = 8.99 Å) of Cs_2GeF_6. A little doping of Mn^{4+} does not change the crystal structure of this Cs_2GeF_6 host. Fig. 1(b) illustrates the crystal structure of Cs_2GeF_6 unit cell viewed in [110] direction, each Ge^{4+} is coordinated with six F^- to form a regular GeF_6^{2-} octahedron. Because Mn^{4+} not only has the same valence state as Ge^{4+}, but also the identical ionic radius with Ge^{4+} (0.53 Å, CN = 6 *vs.* 0.53 Å, CN = 6), Mn^{4+} in $Cs_2GeF_6:Mn^{4+}$ will occupy the site of Ge^{4+} in the centre of octahedron.

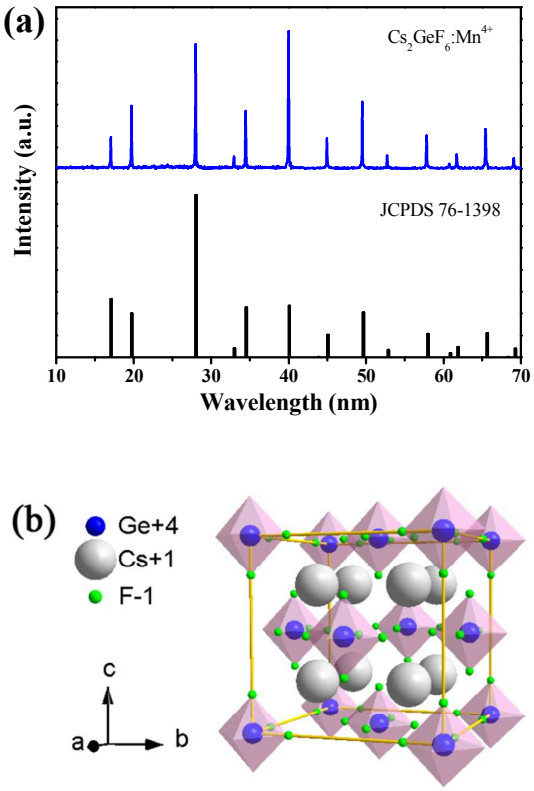

Fig.1 (a) XRD pattern of the $Cs_2GeF_6:Mn^{4+}$ and (b) crystal structure of Cs_2GeF_6 unit cell viewed in [110] direction

The morphology and composition of the obtained $Cs_2GeF_6:Mn^{4+}$ were examined by SEM and EDS analysis, and the representative results are shown in Fig. 2. Obviously, the obtained products exhibit an irregular morphology with smooth surfaces. Closely inspecting the particle size distribution among them, it can be found that the $Cs_2GeF_6:Mn^{4+}$ product displayed an apparent larger size (~ 30 μm).Compared with $Cs_2GeF_6:Mn^{4+}$ prepared by chemically etching Ge shots,[18] obvious edges and corners can be found from our sample, this result shows that the sample has been well crystallized.[22] Fig. 2b is the corresponding EDS spectrum. These peaks belong to F, Ge, Cs, and Mn elements, respectively. This result indicates that Mn element has been indeed doped into the matrix lattice to occupy the lattice site of Ge. The peak of Si element in Fig. 2b is due to the silicon wafer used during the measurement of SEM and EDS. Moreover, the absence of oxygen peak in these EDS spectra implies that there is no MnO_2 produced during this precipitation process.[23]

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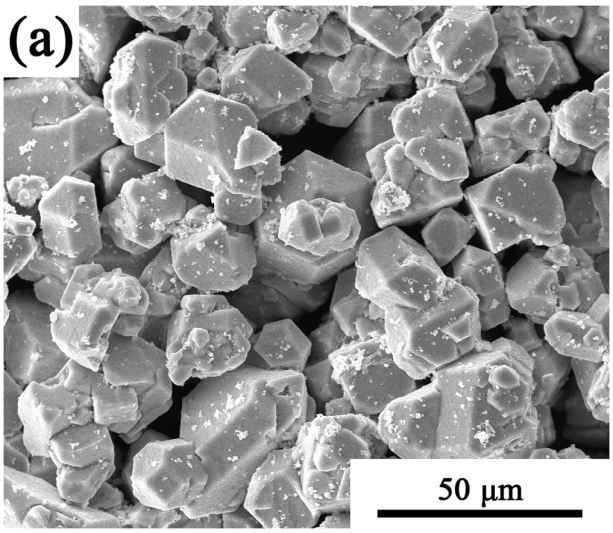

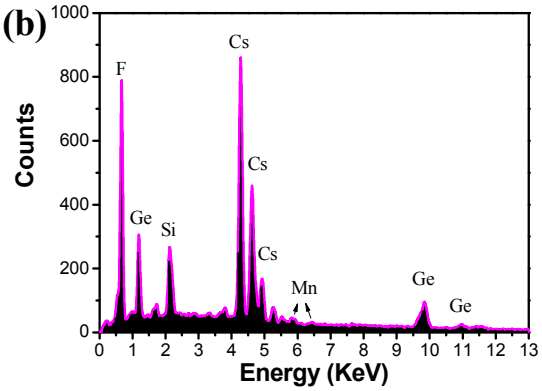

Fig.2 (a) SEM image and (b) EDS spectrum of the Cs_2GeF_6: Mn^{4+}

Optical properties

The diffuse reflectance spectra of Cs_2GeF_6 and Cs_2GeF_6:Mn^{4+} are shown in Fig. 3. Comparing with Cs_2GeF_6 host, Cs_2GeF_6:Mn^{4+} exhibits two obvious absorption bands at ~ 350 nm and ~ 455 nm in Fig. 3b, which are due to the absorption of Mn^{4+} in Cs_2GeF_6:Mn^{4+}. Fig. 3c is the excitation spectrum of Cs_2GeF_6:Mn^{4+} by monitoring 633 nm emission. Two broad excitation bands located at ~ 350 nm and ~ 455 nm, which can be assigned to the spin-allowed transitions of Mn^{4+} from the ground state $^4A_{2g}$ to the excited states $^4T_{1g}$ and $^4T_{2g}$, respectively. This result is in agreement with that of DRS spectrum of Cs_2GeF_6:Mn^{4+}. The strongest excitation band of Cs_2GeF_6:Mn^{4+} is located at ~ 455 nm, which just meets with the emission wavelength (λ = ~ 450 nm) of GaN blue LED chip.

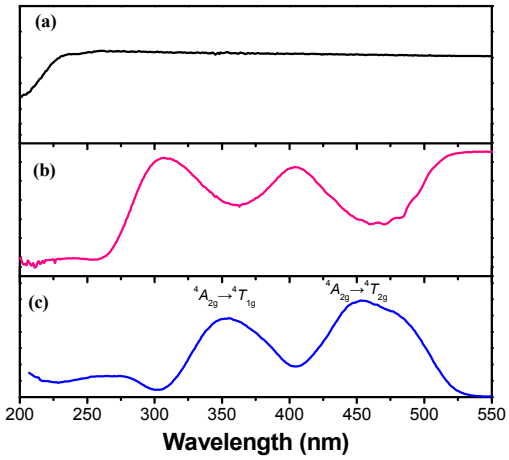

Fig. 3 Diffuse reflectance spectra of (a) Cs_2GeF_6 and (b) Cs_2GeF_6:Mn^{4+}, (c) excitation spectrum of Cs_2GeF_6:Mn^{4+}

Fig. 4 is the emission spectra of Cs_2GeF_6:Mn^{4+} excited by 455 nm light at 293 K and 12K. The as-prepared sample exhibited intense red emission at 12 K, which is due to the spin-forbidden $^2E_g \rightarrow {}^4A_{2g}$ transition of Mn^{4+}. The series of emission peaks located at ~ 615, 624, 633, 636, 649 nm are ascribed as the transitions of the v_6, zero phonon line (ZPL), v_6, v_4, v_3 vibronic modes, respectively.[18] Weaker ZPL emission of the phosphor can be found from the emission spectrum at 12 K. At 293 K, the ZPL emission of Cs_2GeF_6:Mn^{4+} disappears, and new emission peak (v_4) at 611 nm appears in the emission spectrum. This result is in accordance with that reported by S. Adachi. [18] Bright red light can be observed form this sample excited by ~ 460 nm blue light. The CIE (Commission Internationale de l'Eclairage, International Commission on Illumination) chromaticity coordinates according to the emission spectrum of Cs_2GeF_6:Mn^{4+} are calculated to be (x = 0.69, y = 0.31), which are very close to the NTSC (National Television Standard Committee) standard values for red (x = 0.67, y = 0.33). To ensure the luminous efficiency (LE) of the as-prepared phosphor, the luminescent property of commercial K_2TiF_6:Mn^{4+} red phosphor was investigated, compared with that of Cs_2GeF_6:Mn^{4+}. Commercial K_2TiF_6:Mn^{4+} share the similar emission spectrum with that of Cs_2GeF_6:Mn^{4+}, except for little blue-shift of emission positions. The emission intensity of as-prepared Cs_2GeF_6:Mn^{4+} is about 1.14 times than that of commercial K_2TiF_6:Mn^{4+}.

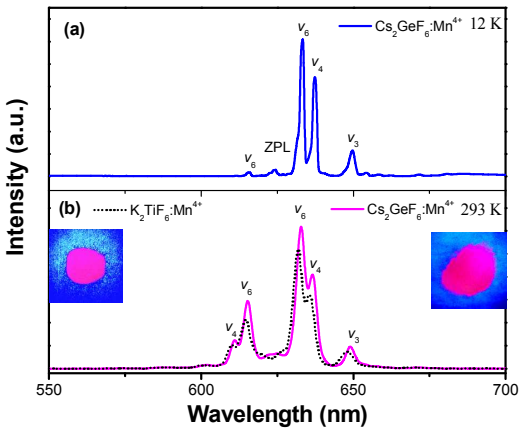

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Fig. 4 Emission spectra of the Cs_2GeF_6:Mn^{4+} and K_2TiF_6:Mn^{4+} (a) at 12 K and (b) 293 K.

In order to investigate the influence of Mn^{4+} content on the PL properties, a series of Cs_2GeF_6:Mn^{4+} prepared with the different molar ratios of GeO_2 and K_2MnF_6 were synthesized, and their emission spectra are shown in Fig. 5. All the emission spectra are of similar sharps with five main emission peaks from 600 nm to 650 nm. With the increasing of K_2MnF_6 consumption, the emission intensity of Cs_2GeF_6:Mn^{4+} is increasing. When the molar ratio of GeO_2 and K_2MnF_6 is 10:1, the as-obtained sample is of the strongest emission intensity. In order to confirm the concentration quenching phenomenon of Mn^{4+} in Cs_2GeF_6:Mn^{4+}, atomic adsorption spectrophotometer was adopted to measure the relative concentration of Mn^{4+}, and the results were presented in Table S1. With the increasing of K_2MnF_6 consumption, the concentration of Mn^{4+} in Cs_2GeF_6:Mn^{4+} is also increasing. Fig. S1 is concentration dependence of the relative emission intensity of Mn^{4+} $^4A_{2g}\rightarrow{}^4T_{2g}$ transition in Cs_2GeF_6:Mn^{4+}. When the concentration of Mn^{4+} is 8.78 %, the emission intensity is the strongest among these phosphors.

According to Dexter and Schulman,[24] the critical concentration of the concentration quenching can be used as a measure of the critical distance (R_c) of energy transfer. The R_c values can be practically calculated using the following equation:

$$R_c = 2\left(\frac{3V}{4\pi x_c N}\right)^{\frac{1}{3}} \quad [1]$$

where x_c is critical concentration, N is the number of Mn^{4+} ions in the unit cell and V is the volume of the unit cell. In this case, x_c is 0.0878, N is 4, and V is 726.57Å^3. The calculated R_c value is about 15.8 Å for substitution of Mn^{4+} at the Ge^{4+} site. From this value, the critical distance (R_c) of energy transfer was larger than the distance (R) between the Mn^{4+} ions (R value is about 1.7980 Å, seeing ICSD 35547); as it can be seen that $R< R_c$, it is presumed that energy transfer between Mn^{4+} ions dominate in the case of Cs_2GeF_6:Mn^{4+} phosphor.

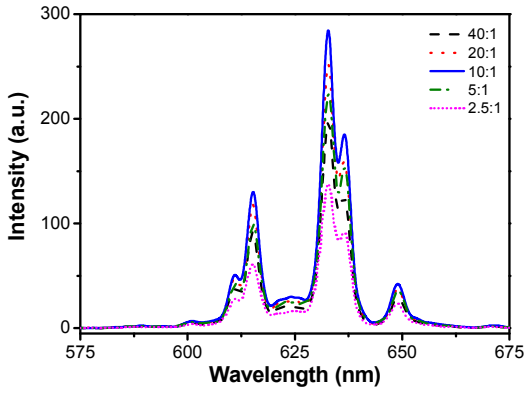

Fig. 5 Emission spectra of Cs_2GeF_6:Mn^{4+} prepared with the different molar ratios of GeO_2 and K_2MnF_6

Since LEDs are fabricated and work usually at a temperature below 150 °C,[25] the thermal stability and the temperature dependence on luminous efficiency are important parameters for phosphors. As shown in Fig. 6, TG and DSC curves of Cs_2GeF_6:Mn^{4+} show that its thermal decomposition temperature (T_d) is about 450 °C. Such high decomposition temperature suggests that this phosphor has high thermal stability and it is enough to be applied in WLED devices.

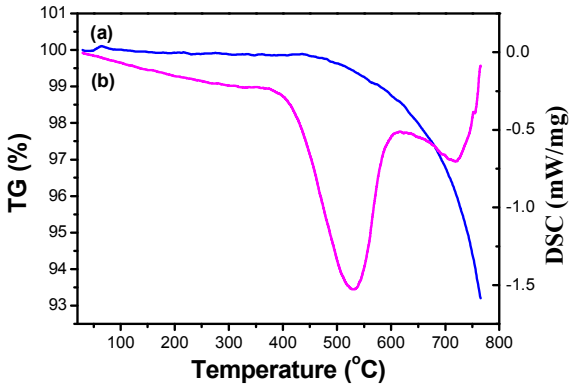

Fig. 6 (a) TG and (b) DSC curves of Cs_2GeF_6:Mn^{4+}

Fig.7 exhibits the emission spectra of Cs_2GeF_6:Mn^{4+} under different temperature. All the emission peaks are in the same positions with the strongest emission peak at ~ 633 nm, no obvious emission peak position shift can be found. The inserted figure in Fig.7 is the temperature dependence of the relative emission intensity of Cs_2GeF_6:Mn^{4+}. The integrated intensity of the sample at 140 °C is still higher than that of the sample at room temperature, which indicates that this red phosphor shared high thermal stability. And this result is in according with that of Rb_2SiF_6:Mn^{4+}.[22]

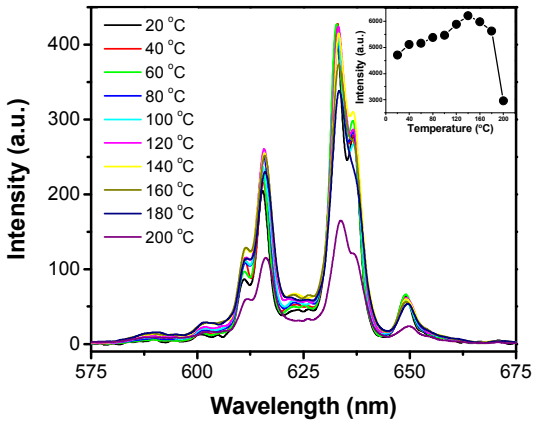

Fig.7 Emission spectra of Cs_2GeF_6:Mn^{4+} under different temperature.

Fig. S2 shows the decay curve for $^2E_g\rightarrow{}^4A_{2g}$ (633 nm) of the Mn^{4+} in Cs_2GeF_6:Mn^{4+} red phosphor. This decay curve is well fitted into single-exponential function, and the lifetime τ value of Cs_2GeF_6:Mn^{4+} is 8.8 ms. This result complements the experimental data of previous reports prepared by other methods.

Performance of LED Devices

Fig. S3 is the EL spectra of the LED chip and red LED based on Cs_2GeF_6:Mn^{4+} under 20 mA current excitation. The emission of GaN LED chip is at ~ 450 nm, and its half-peak width is about 20 nm. Compared with curve a, the emission of LED chip gets

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weak in curve b, indicating that $Cs_2GeF_6:Mn^{4+}$ can efficiently absorb the emission of LED chip. The red emission between 600 and 650 nm is due to the $^2E_g \rightarrow {}^4A_{2g}$ transition of Mn^{4+} in $Cs_2GeF_6:Mn^{4+}$. Bright red light can be observed from this red LED based on $Cs_2GeF_6:Mn^{4+}$. Fig. 8 is the EL spectra of WLEDs with YAG. The broad band in blue region is due to the emission of GaN chip, and the greenish yellow emission is due to the emission of YAG and different amount of $Cs_2GeF_6:Mn^{4+}$. Since the emission of YAG in red regions is very weak, this WLED based on YAG exhibits high T_c (6090 K) and low R_a (72.7). With the introduction of $Cs_2GeF_6:Mn^{4+}$, red emission peaks can be observed obviously at ~ 615, 624, 633, 636, 649 nm, which are due to the $^2E_g \rightarrow {}^4A_{2g}$ of Mn^{4+}. And the emission of LED chip turns weaker. The related parameters of these WLED are list in Table 1. When the amount of $Cs_2GeF_6:Mn^{4+}$ was adjusted from 5 % to 20 %, the examined T_c of the WLEDs was dropped from 5193 to 3673 K, and *Ra* was improved from 75.2 to 84.9. This performance of the WLEDs can satisfy the requirement of indoor lighting. The corresponding CIE coordinates were shown in Fig. 9, which revealed that the T_c moved to warm white region with the increasing of red colour component.[10] According the survey of X.Y. Chen, et.al, warm WLEDs based on red phosphors doped Mn^{4+} with a luminous efficacy higher than 90 lm/W had never been achieved before they fabricated the warm WLED based on $K_2TiF_6:Mn^{4+}$ (LE = 124 lm/W)under 20 mA current excitation.[9] In this work, we fabricated high-performance warm WLED based on $Cs_2GeF_6:Mn^{4+}$ with low T_c (3673 K), high R_a (84.9), and high LE (141.5 lm/W). Bright white light can be observed by naked eyes from this WLED, when it was excited with 20 mA current. These results demonstrated that this red phosphor share excellent PL properties, which can find potential application in warm WLEDs.

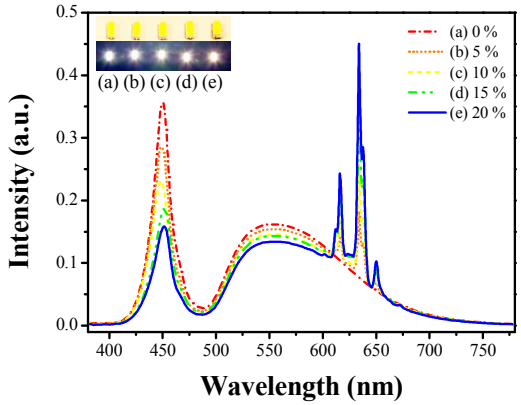

Fig. 8 EL spectra of WLEDs based on YAG and different amount of $Cs_2GeF_6:Mn^{4+}$ udner 20 mA current excitation

Table 1 Performance of the WLEDs with different amount of $Cs_2GeF_6:Mn^{4+}$ at 20 mA forward current.

Device	$Cs_2GeF_6:Mn^{4+}$ *(wt/%)**	T_c(K)	*Ra*	CIE(*x*, *y*)	LE (lm/W)
a	0	6090	72.7	(0.321, 0.329)	158.9
b	5	5193	75.2	(0.340, 0.344)	153.9
c	10	4567	77.2	(0.358, 0.359)	147.2
d	15	4081	82.0	(0.377, 0.375)	144.3
e	20	3673	84.9	(0.395, 0.383)	141.5

* $wt/\% = \frac{m_{(Cs_2GeF_6:Mn^{4+})}}{m_{(epoxy\ resin)}} \times 100\ \%$

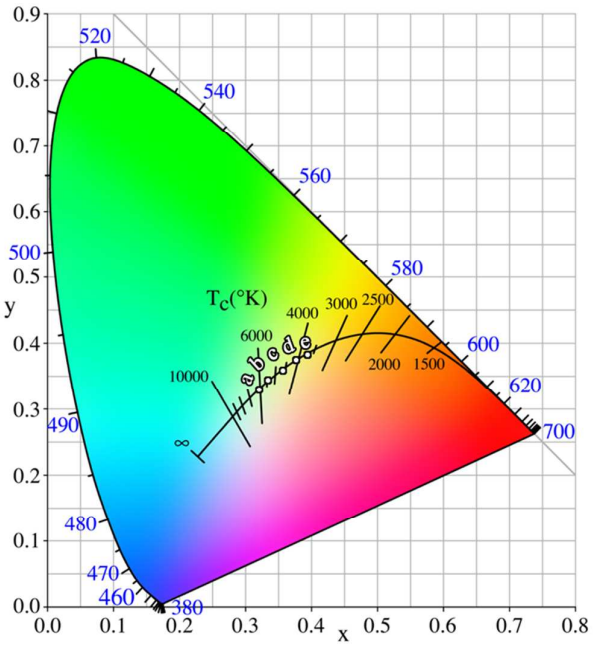

Fig. 9 Chromaticity coordinates of WLEDs fabricated with different amount of $Cs_2GeF_6:Mn^{4+}$ in CIE 1931

Conclusions

Red phosphor $Cs_2GeF_6:Mn^{4+}$ was prepared by the cation exchange method, and their structure, morphology and optical properties were investigated. The as-prepared phosphor $Cs_2GeF_6:Mn^{4+}$ with high thermal stability shows the intense and broad excitation band in blue-light region, and red emission with appropriate CIE coordinates (x = 0.69, y = 0.31). The WLEDs fabricated with $Cs_2GeF_6:Mn^{4+}$ and commercial YAG show exhibits intense white light with good optical performances (T_c = 3673 K, R_a = 84.9, LE = 141.5 lm/W). Hence, $Cs_2GeF_6:Mn^{4+}$ is a promising red phosphor for warm WLEDs.

Acknowledgements

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Technology) in University of Yunnan Province (2011UY09) and Yunnan Provincial Innovation Team (2011HC008).

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