

Journal of Materials Chemistry C

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A new and efficient red phosphor for solid-state lighting: $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$

Received 00th July 2015,
Accepted 00th August 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

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$\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ powders as a novel red phosphor has been successfully fabricated in large scale through cation exchange method using K_2MnF_6 as Mn^{4+} source at ambient temperature. The $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ product is well crystallized into single-phase with hexagonal micro-rod morphology and presents sharp red emissions under blue light illumination. It can significantly improve Ra and CCT levels of YAG type white LED used for indoor lighting.

Introduction

Rare earth phosphors are crucial manufacturing components of light-emitting diodes (LEDs) used in current solid-state lighting system.¹⁻³ Red emission complements of commercial $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG) type WLEDs have attracted much attention because of their ability to compensate the widely known insufficiency of high correlated colour temperature (CCT > 4000 K) and low color rendering index (CRI, Ra < 80).^{4,5} Rare-earth-activated sulfides and nitrides are often employed as red components for the fabrication of fascinating warm WLEDs.^{6,7} However, their broadband emissions beyond 650 nm decrease the luminous efficiency and the sensitivity of human eyes.⁸⁻¹⁰ Recently, much effort has been devoted to the exploration of Mn^{4+} doped fluoride red phosphors by maturely controlling the formation of Mn^{4+} and constructing different fluoride matrixes.

Mn^{4+} activated red fluoride phosphors exhibit broadband absorption and narrowband emission in the blue and red regions since its distinct *d-d* transitions.^{11,12} Mn^{4+} is sensitive to surrounding environment and hard to be controlled. Hence, there are many reports to synthesize Mn^{4+} doped fluoride complexes, such as $\text{Na}_2\text{TiF}_6:\text{Mn}^{4+}$ and $\text{K}_2\text{TiF}_6:\text{Mn}^{4+}$.^{13,14} In our previous work, the synthesis and photoluminescence (PL) properties of a series of fluoride red phosphors, such as $\text{BaGeF}_6:\text{Mn}^{4+}$, $\text{Na}_2\text{XF}_6:\text{Mn}^{4+}$ (X = Si, Ti and Ge) have been

demonstrated.^{15,16} However, to the best of our knowledge, the formation of $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ red phosphor has not been reported.

In this work, we present the synthesis and PL properties of a new fluoride red phosphor $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$, with broad blue-absorption and intense red-emission bands, which may has the potential to improve the CCT and CRI levels of an indoor lighting WLED.

Experimental

Materials. All source materials in this work, including hydrofluoric acid, cesium fluoride, potassium permanganate, titanium dioxide, hydrogen peroxide and potassium hydrogen bifluoride were of analytical grade and without any further purification prior to use. The YAG yellow phosphor was commercially purchased from Shenzhen Quanjing Photon Co. Ltd., China.

Synthesis of K_2MnF_6 precursor and $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ products. Mn^{4+} source K_2MnF_6 was synthesized according to the method described in the literature.¹⁷ Specifically, 20 g KHF_2 and 2 g KMnO_4 were dissolved in HF (40 %) solution. The yellow powder K_2MnF_6 was precipitated by slowly dropping H_2O_2 (30 %). After fast filtering and washing by acetone, the yellow powder was oven-dried at 80 °C for 1.0 h.

In a typical synthesis, we started with a 50 ml plastic beaker containing 10 ml magnetically stirring 40 % HF solution in which 0.3994 g (5 mmol) TiO_2 was added until completely dissolved. Then 0.1236 g (0.5 mmol) K_2MnF_6 and 1.6709 g (11 mmol) CsF were put into the colourless transparent solution in order. The formation of $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ phosphor was carried out at room temperature. After 30 min magnetically stirring and a quick cooling process in salt-ice bath, the precipitates were collected, washed with methanol for several times and dried at 80 °C for 1.0 h. For comparison, $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ red phosphor samples were synthesized with different initial mole ratios between TiO_2 and K_2MnF_6 (40:1, 20:1, 10:1, 5:1 and 2.5:1).

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† Electronic Supplementary Information (ESI) available: Details to the decay curve, thermogravimetric curve, and influence of different molar ratio of starting materials on the PL properties of $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ phosphor, as well its WLED performance data. See DOI: 10.1039/x0xx00000x

Fabrication of LEDs. The commercial YAG yellow phosphor, different amount of $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ red phosphor and blue GaN chip were used to fabricate LEDs. The phosphors were mixed with epoxy resin thoroughly. The obtained phosphor-epoxy resin mixture was coated on the surface of the GaN chip. The fabricated LEDs were operated at a forward current of 20 mA.

Characterization. Initially, the crystal structure of the as-prepared product was investigated by powder X-ray diffraction (XRD) with a Panalytical X'pert Pro Multi-purpose X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ 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 a Cary 5000 UV-Vis-NIR spectrophotometer and an Edinburgh FLS920 combined fluorescence lifetime and steady state spectrometer with a 450 W xenon lamp and 60 W μF flash lamp, respectively. PL properties were examined on a Cary Eclipse FL1011M003 (Varian) spectrofluorometer with the excitation and emission slits 2.5 nm, and the xenon lamp was used as excitation source. The low temperature emission spectrum (12 K) was measured using a Xe lamp connected with a monochromator. The sample temperature is controlled by a temperature controller (YANGMING XMTG-6311). The performance of WLEDs was recorded on a high accurate array spectrometer (HSP6000).

Results and discussion

Morphology and compositional analysis

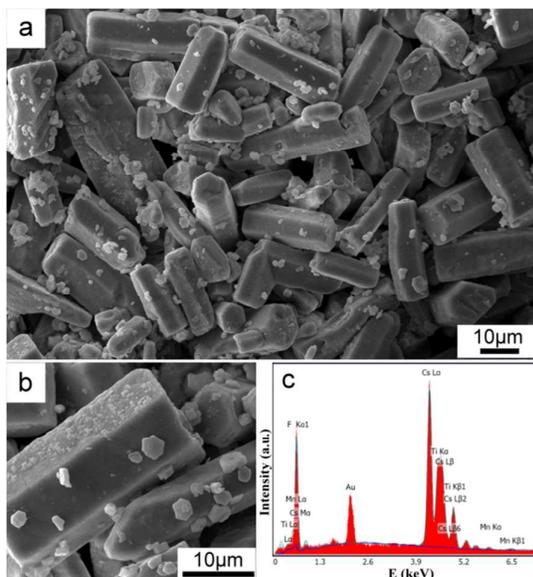


Fig. 1 (a, b) SEM pictures and (c) EDS spectrum of the as-synthesized $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ product.

Fig. 1 shows the representative morphology and composition results of the obtained $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ product examined from SEM and EDS measurements. In Fig. 1a, a close-up view shows that the sample is composed of a number of hexagonal prismatic crystals with clear edges and corners, as well tiny particle on its smooth surfaces, indicating the product has been well crystallized.^{18,19} Closely view the tips of a typical hexagonal prism in Fig. 1b, its height is about $30\ \mu\text{m}$ and two parallel symmetrical hexagons are base surfaces with side length of about $6\ \mu\text{m}$. The corresponding EDS spectrum in Fig. 1c recognized the existence of F, Ti, Cs, and Mn elements, as well the absence of O, suggesting that Mn^{4+} has successfully occupied the lattice site of Ti^{4+} and no MnO_2 was produced. Actually, the doping amount of Mn^{4+} in this sample, measured from AAS system, is 3.97%. Of course, with the various molar ratios between TiO_2 and K_2MnF_6 , different doping amount of Mn^{4+} in Cs_2TiF_6 matrix can be obtained. The results are displayed in Tab. 1. Moreover, the prepared $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ powders were found to be a bright yellow color observed by naked eyes.

Tab. 1 AAS results of $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ red phosphors prepared from different molar ratio between TiO_2 and K_2MnF_6 .

Samples	Molar ratios of $\text{TiO}_2:\text{K}_2\text{MnF}_6$	Doping amount of Mn^{4+} (mol %)
1	40:1	1.33
2	20:1	2.21
3	10:1	3.97
4	5:1	7.94
5	2.5:1	14.02

More detailed crystal structural studies on the fabricated $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ product along with the pure Cs_2TiF_6 matrix and K_2MnF_6 source were carried out by XRD, and the results are exhibited in Fig. 2. In curve a, all peaks belong to hexagonal K_2MnF_6 crystal, implying the preset Mn^{4+} source is pure single-phase. Comparing curves 2b and c, we can found all the diffracted peaks can be well indexed to the space group $P-3m1$ of hexagonal Cs_2TiF_6 crystal (JCPDS No. 51-0612, $a = b = 6.167\ \text{\AA}$, $c = 4.999\ \text{\AA}$), and no traces of K_2MnF_6 residual and other secondary phase were identified. This indicates the cation exchange result of Mn^{4+} substituting for Ti^{4+} does not alter the crystal structure of Cs_2TiF_6 matrix. That is because Mn^{4+} not only has the identical valence state, but also the similar ionic radius as Ti^{4+} ($0.530\ \text{\AA}$, CN = 6 vs. $0.605\ \text{\AA}$, CN = 6), which is beneficial for Mn^{4+} ions replacing the octahedral core sites of Ti^{4+} to coordinate with 6 F^- anions forming stable MnF_6^{2-} octahedron in Cs_2TiF_6 crystal field, in which each Ti^{4+} coordinates with 6 F^- to form a regular TiF_6^{2-} octahedron and Cs^+ ion is at the centre of 12 neighbouring F^- anions.

Optical properties

It has been well accepted that the un-doped fluoride host absorb little in the visible region whilst Mn^{4+} -doped fluoride phosphor presents broad absorption and intense emission in

the blue and red regions, respectively.²⁰ Fig. 3a shows the photoluminescence excitation (PLE) and DRS results of the

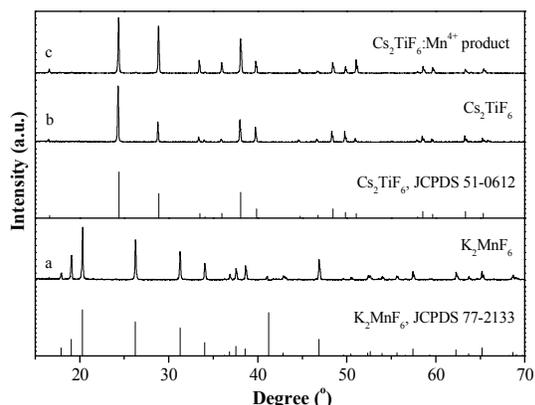


Fig. 2 Representative XRD patterns of (a) K_2MnF_6 , (b) Cs_2TiF_6 matrix and (c) $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ product.

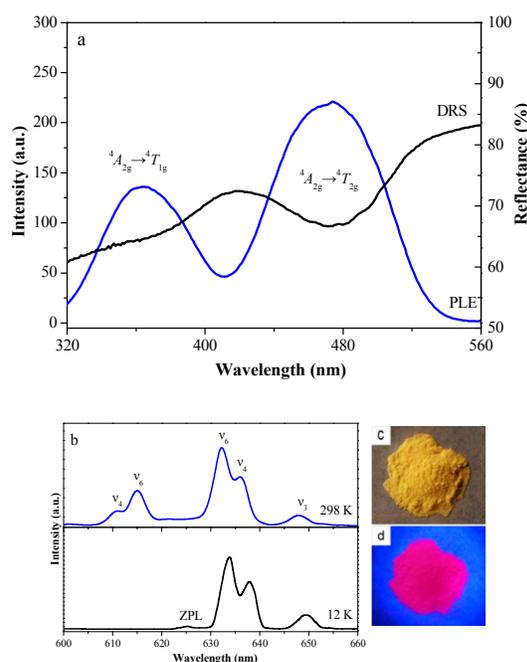


Fig. 3 $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ phosphor: (a) PLE and DRS results. (b) PL spectra examined at room and low temperature, respectively. Photographs under (c) natural light and (d) 460 nm blue light.

above $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ product. The PLE spectrum, monitored at 632 nm, is composed of two broad bands with peaks at 363 nm and 474 nm, which locating in the larger wavelength area than those of the previously reported $\text{Na}_2\text{TiF}_6:\text{Mn}^{4+}$ and $\text{K}_2\text{TiF}_6:\text{Mn}^{4+}$ phosphors.^{13,14} That is because the excitation peak position is highly dependent on the crystal field strength.²¹ $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ has the same TiF_6^{2-} ion group as $\text{Na}_2\text{TiF}_6:\text{Mn}^{4+}$ and $\text{K}_2\text{TiF}_6:\text{Mn}^{4+}$ while Cs^+ presents much larger radius than that of Na^+ and K^+ , which means Cs_2TiF_6 possesses larger unit cell

volume than Na_2TiF_6 and K_2TiF_6 , leading to its weaker crystal field strength and hence obvious red shift excitation wavelength. Furthermore, the two broad peaks can be attributable to the spin-allowed transitions of Mn^{4+} from ground state ${}^4A_{2g}$ to excited states ${}^4T_{1g}$ and ${}^4T_{2g}$, respectively.²² The DRS result noticeably reveals a strong absorption in the same region with a maximum at 474 nm, which is perfectly in accordance with the above strongest excitation wavelength at 474 nm.

The PL properties of $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ phosphor were examined at different temperatures and Fig. 3b show two representative PL spectra recorded at room and low temperature respectively. At $t = 25^\circ\text{C}$, the red emissions originate from the spin-forbidden ${}^2E_g \rightarrow {}^4A_{2g}$ transition. The five peaks are due to the transitions of anti-Stokes v_4 , v_6 and Stokes v_6 , v_4 and v_3 vibronic modes respectively, in which ZPL emission is hardly observed.²³ At low temperature, ZPL emission can be clearly observed, and anti-Stokes lines of v_4 and v_6 disappear. These features are the same as those observed in $\text{K}_2\text{GeF}_6:\text{Mn}^{4+}$ phosphor.²⁴ The characteristics of blue-excitation and red-emission for the $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ phosphor meet well with the emission wavelength of blue chip and the red component need of YAG type WLED. Actually, the sample shows a uniform yellow tint under natural light illumination (Fig. 3c) which emits brilliant red light under blue light (460 nm) excitation (Fig. 3d). Its decay curve is well fitted into single-exponential function with a lifetime τ value of 3.78 ms (Fig. S1 in ESI†).

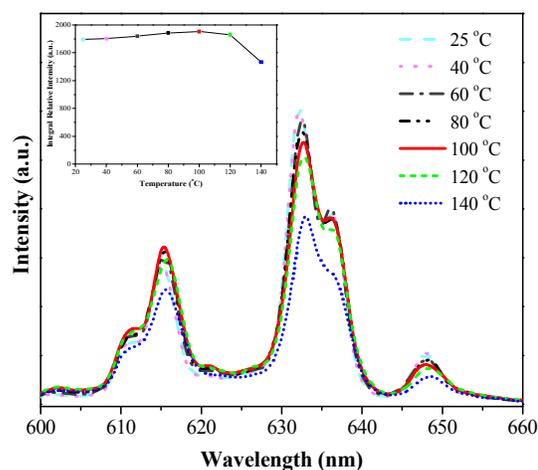


Fig. 4 Temperature-dependent thermal luminescent spectra of $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ red phosphor and relative intensity of emission spectrum by integrating the spectral area.

The influence of temperature on the PL properties is shown in Fig. 4. Obviously, with the temperature increasing, it can be found that the emission peak position does not shift. Up to 100°C , over 100 % of the integral emission intensity can be preserved compared with that at 25°C . Actually, the $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ red phosphor is very stable chemically and it cannot be decomposed until 400°C (Fig. S2 in ESI†). Furthermore, the influence of Mn^{4+} doping amount on the PLE

and PL properties have been investigated and the results can be optimized (Fig. S3 in ESI[†]). The optimal doping is about 4%.

Due to the excellent properties of the new red phosphor, that is Cs₂TiF₆:Mn⁴⁺, it is necessary to investigate the illumination performance of its devices. A series of WLEDs were fabricated by merging YAG, various amount of Cs₂TiF₆:Mn⁴⁺ and epoxy resin on blue GaN chips (~450nm). Their chromaticity coordinates are labelled in or close to the white light region in CIE 1931 colour spaces as colour points of i-vi in Fig. 5b. Photographs of the lighting WLEDs are shown in the insert image of Fig. 5a. Consistent with the decrease of CCT, a noticeable warmer tone of the emitting light can be observed, owing to the increase of red light in the emission spectrum. Their EL spectra reconfirm the sharp emission lines of Cs₂TiF₆:Mn⁴⁺ phosphor and more red components with the lower CCTs. Fig. 5c shows the bright red light of a typical red LED based on Cs₂TiF₆:Mn⁴⁺ phosphor. Tab. S1 in ESI[†] compares the CCT, CRI and luminous efficiency data of these WLEDs. Evidently, by adding Cs₂TiF₆:Mn⁴⁺ phosphor into the YAG powders, warm white light with R_a > 80 and CCT < 4000 K can be readily achieved. The R_a and CCT of the warmest WLED are 80.1 and 3272 K with an excellent luminous efficiency of 124.6 lm·W⁻¹. Notably, this luminous efficiency value is much higher than the previous reports.

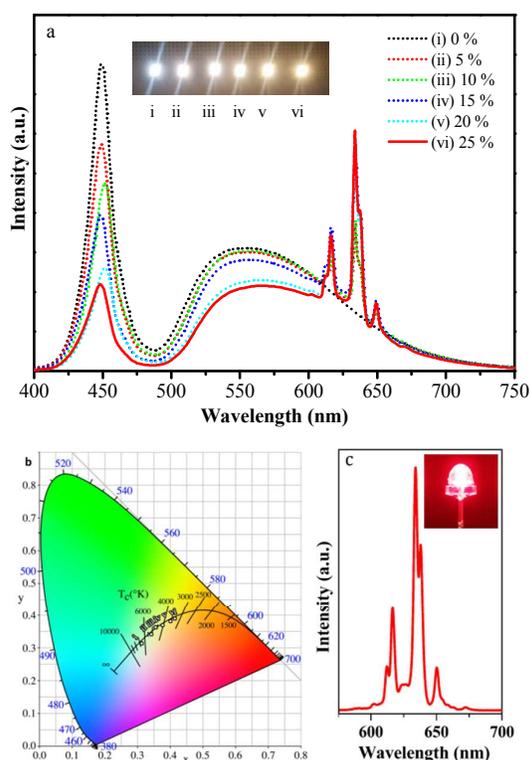


Fig. 5 (a) Electroluminescent (EL) spectra and photographs of five WLEDs. (b) Their chromaticity coordinates in CIE 1931 color spaces. (c) EL spectrum and photograph of a red LED. All the LEDs were recorded under 20 mA drive current.

Conclusions

In conclusion, a novel Cs₂TiF₆:Mn⁴⁺ red phosphor, belonging to hexagonal *P-3m1* crystal structure, has been successfully prepared through cation exchange route. The Cs₂TiF₆:Mn⁴⁺ product is well crystallized into single-phase with hexagonal micro-rod morphology. The Cs₂TiF₆:Mn⁴⁺ phosphor can absorb broadband blue light and emit intense bright narrow band red light efficiently. Therefore, with the addition of Cs₂TiF₆:Mn⁴⁺ red phosphor, obvious improvement in CRI and CCT data has been achieved, resulting in the Cs₂TiF₆:Mn⁴⁺ phosphor can be a potential candidate for the indoor lighting WLEDs.

Acknowledgements

Financial supports from the National Natural Science Foundation of China, the Natural Science Foundation of Yunnan Province (Grants 21261027 and 2014FB147) are gratefully acknowledged. We appreciate Dr. H. L. Tam from Hong Kong Baptist University for the low temperature emission spectrum. M. M. Wu acknowledges the Joint Funds of the National Natural Science Foundation of China and Guangdong Province, Research Fund for the Doctoral Program of Higher Education of China and Guangdong Province for industrial applications of rare earth materials (U1301242, 20130171130001 and 2012B09000026).

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Graphical Abstract

A new red phosphor $\text{Cs}_2\text{TiF}_6:\text{Mn}^{4+}$ has been prepared by a facile cation exchange route, which can absorb broad blue band and emit intense red light efficiently, and can be a potential candidate for its application in indoor lighting WLEDs.

