Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

High-Performance Ultra-Narrow-Band Green-Emitting Phosphor $LaMgAl_{11}O_{19}:Mn^{2+}$ for Wide Color-Gamut WLEDs Backlight Display

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Electronic Supplementary Information (ESI):

Experimental section

Synthesis

A series of LMAO:Mn^{2+} phosphors samples were successfully synthesized by a easily operated solid-state reaction method. According to the nominal chemical compositions, weighed La_2O_3 (99.99%), MgO (99.9%), $Al(OH)_3$ (99.99%), and MnO_2 (AR) by stoichiometry and grinded them thoroughly with ethyl alcohol in an agate mortar for 30 minutes. Furthermore, the well grinded and mixed raw materials were transferred to aluminum crucibles and calcined at 1500 °C for 6 h in air atmosphere. As a reference, some well grinded and mixed raw materials were calcined at 1500 °C for 6 h in 10%H_2/90%N_2. After firing, the samples were cooled to room temperature and the final products were obtained.

Characterization

The purity of the phases of all samples was analyzed by X-ray powder diffraction (XRD) using a Bruckner D8 Advance diffractometer with Cu-Kα radiation (λ= 1.54145 Å). The XRD data were collected in a 2θ range from 10° to 80° with the continuous scan mode at the speed of 0.80 s per step with step size of 0.01° for the refined sample. XRD Rietveld refinement of the sample was performed by Topas software. The morphology of as-synthesized phosphors was observed by scanning electron microscopy (SEM, ZEISS Merlin Compact, Germany). Energy dispersive X-ray spectrometry (EDS) was employed to measure the composition of the sample, which was attached to the SEM. The diffuse reflection spectrum was collected by a UV-3600 UV-vis-NIR spectrometer (Shimadzu, Japan) using the white powder $BaSO_4$ as a standard material. The excitation and emission spectra as well as the luminescence decay curves were recorded at an Edinburgh FLS1000 combined with a steady-state and fluorescence lifetime spectrometer. The luminescence spectra were excited using a 450 W Xe900 xenon lamp. The quantum yield was measured by the integrating sphere on the Edinburgh FLS 1000 fluorescence spectrometer, and white $BaSO_4$ was employed to be a reference. The luminescence decay curves were measured using a 100 W μF2 μs flash-lamp. The temperature dependent spectra and decay curves were collected using the same instrument attached with a heating equipment (TAP-02). In addition, the white LED was fabricated by mixing the LMAO:0.28Mn^{2+}, K_2SiF_6:Mn^{4+} phosphors with silica gel, and then coated on the blue InGaN LED chip. As for the blue LED chip (λ_{em} = 450 nm), the working voltage of is 2.8-3.2 V and the working current is 5-330mA. The electroluminescence spectrum and optical property parameters of the as-fabricated pc-LED were carried out using the same instrument (FLS1000, Edinburgh).

The absorption efficiency (AE), internal quantum efficiency (IQE) and external quantum efficiency (EQE) of LMAO:0.28Mn^{2+} phosphor were calculated by using the following equations:

$$AE = \frac{\int E_R - \int E_S}{\int E_R}$$

$$IQE = \frac{\int L_S}{\int E_R - \int E_S}$$

$$EQE = AE * IQE = \frac{\int L_S}{\int E_R}$$

in which E_S stands for the spectrum of light used for exciting the phosphor, L_S represents the emission spectrum of the phosphor, and E_R is the spectrum of excitation light without phosphor in sphere.

Results and Discussion

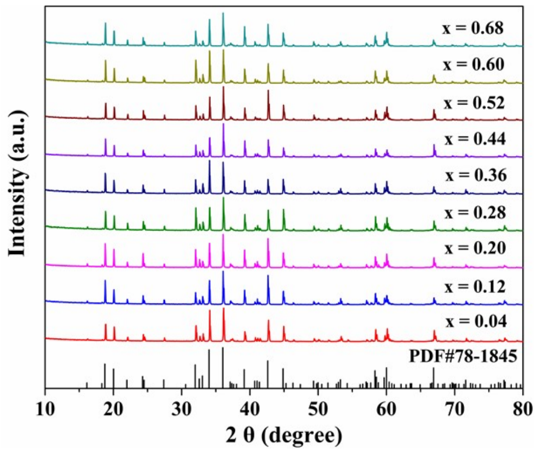

Fig. S1 XRD patterns of LMAO:xMn^{2+} (0.04 ≤ x ≤ 0.68) phosphors.

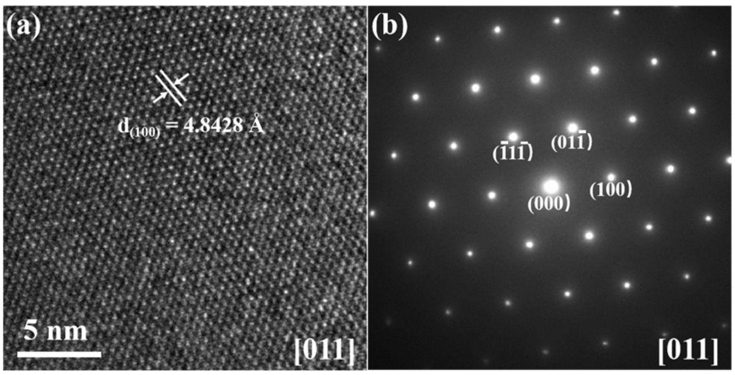

Fig. S2 (a) HRTEM image and (b) SAED pattern of LMAO:0.28Mn^{2+}.

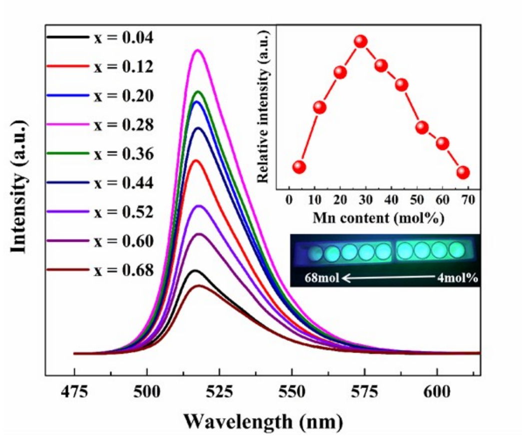

Fig. S3 The emission spectra of the LMAO:xMn^{2+} ($0.04 \le x \le 0.68$) samples; the inset is the digital photo and the intensity of emission peak as a function of Mn^{2+} concentration.

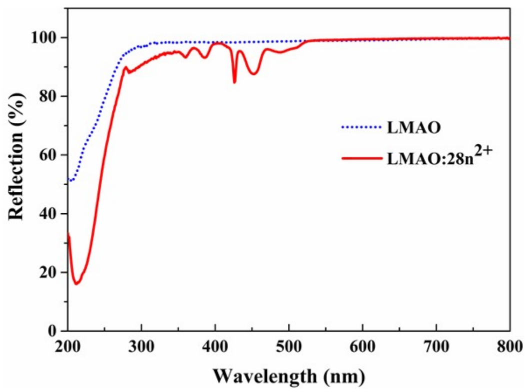

Fig. S4 The diffuse reflection spectrum of LMAO host and LMAO:0.28Mn^{2+}.

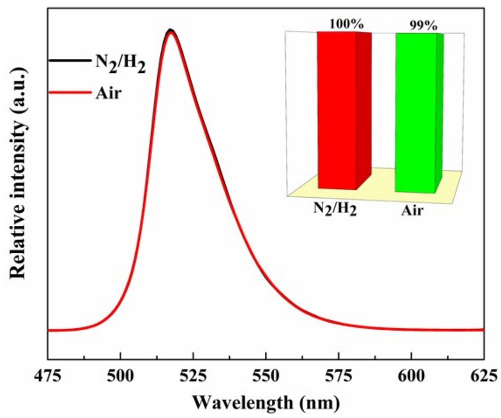

Fig. S5 The emission spectra and the relative intensity (insert picture) of LMAO:0.28Mn^{2+} synthesized in air condition and 10%H_2/90%N_2 atmosphere.

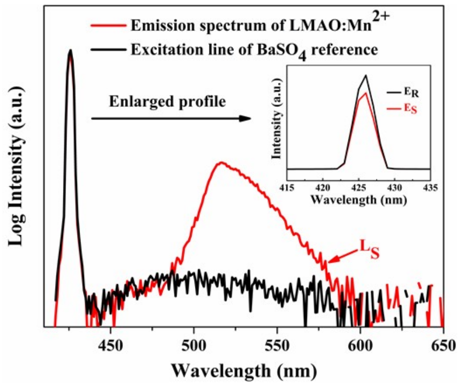

Fig. S6 Excitation line of $BaSO_4$ and the emission spectrum of the LMAO:0.28Mn^{2+} phosphor collected by using an integrating sphere (λ_{em} = 426 nm), the inset shows the magnification for the excitation line of $BaSO_4$ and the emission spectrum of the LMAO:0.28Mn^{2+}.

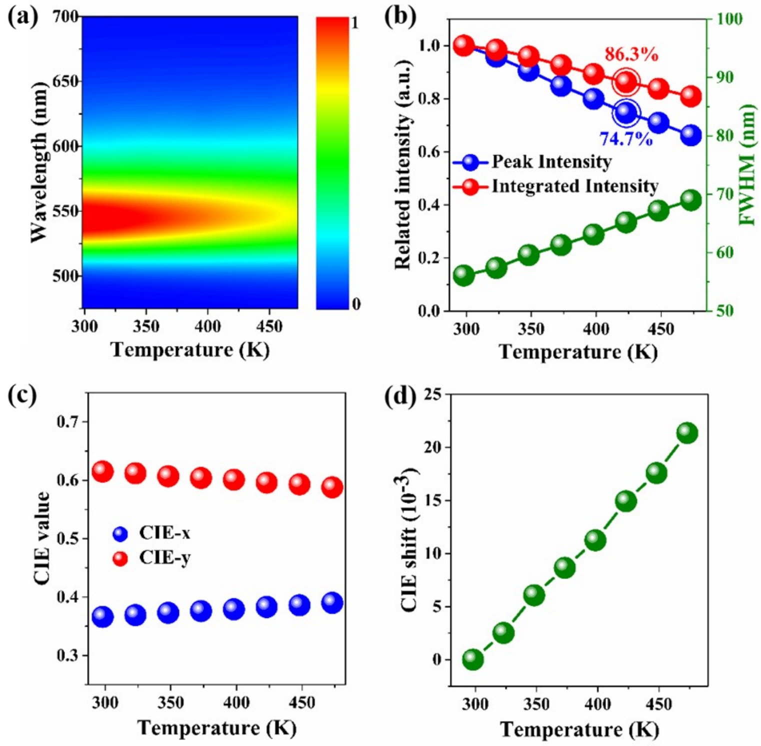

Fig. S7 (a) The temperature-dependent emission intensities of commercial β-SiAlON:Eu^{2+} recorded at temperatures from 298 to 473 K in the wavelength range of 475-700 nm. (b) Normalized integrated intensities, peak intensities, and the variation of FWHM of commercial β-SiAlON:Eu^{2+} depending on increasing temperature. (c) Chromaticity coordinate values and (d) chromaticity shift of commercial β-SiAlON:Eu^{2+} at different temperatures.

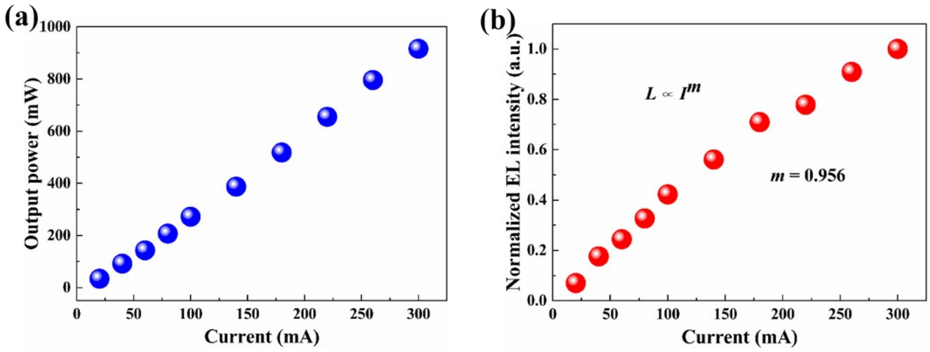

Fig. S8 (a) Output power-current curve and (b) normalized electrofluorescence intensity-current curve of blue LED in the current range 20-300 mA.

Table S1. Crystallographic Data of $LaMg_{0.72}Mn_{0.28}Al_{11}O_{19}$ Derived from Rietveld Refinement of X-ray Diffraction Powder Diffraction Data.

Formula	$LaMg_{0.72}Mn_{0.28}Al_{11}O_{19}$
crystal system	Hexagonal
space group	$P6_3/mmc$ (No.194)
a (Å)	5.5915(7)
c (Å)	21.9742(6)
V (Å^3)	594.9778(1)
formula units per cell	Z = 2
temperature (K)	297
2θ range (°)	10-80
step size (°)	0.01
structure refinement	Topas 5
profile function	PVII
R_{exp}	3.22
R_{wp}	5.16
R_p	3.86
GOF	1.60

Table S2. The comparisons of green phosphors and the color gamut of their phosphor-converted white LED devices using $K_2SiF_6:Mn^{4+}$ as red light in CIE 1931 system.

Phosphor	Peak (nm)	FWHM (nm)	NTSC (%)	Ref.
$SrAl_2Si_2O_8:Mn^{2+}$	517	26	120	[1]
$BaZnAl_{10}O_{17}:Mn^{2+}$	516	31	110	[2]
$MgAl_2O_4:Mn^{2+}$	525	35	116	[3]
$Sr_2Li(Al, Ga)O_4:Eu^{2+}$	512	40	107	[4]
$RbLi_7Si_2O_8:Eu^{2+}$	532	38	112	[5]
$Rb_3Na(Li_3SiO_4)_4:Eu^{2+}$	527	42	103.5	[6]
$Sr_2MgA_{l22}O_{36}:Mn^{2+}$	518	26	127	[7]
$RbNa(Li_3SiO_4)_2:Eu^{2+}$	523	41	113	[8]
$RbLi(Li_3SiO_4)_2:Eu^{2+}$	530	42	107	[9]
β-SiAlON:Eu^2+	540	54	96	[10]
$Ba_2LiSi_7AlN_{12}:Eu^{2+}$	515	61	-	[11]
$Ba[Li_2(Al_2Si_2)N_6]:Eu^2$+	532	57	-	[12]
$SrGa_2S_4:Eu^{2+}$	540	47	86.4	[13]
$CsPbBr_3$	523	23	102	[14]
γ-AlON:Mn^{2+}, Mg^{2+}	520	44	102.4	[15]
$LaMgAl_{11}O_{19}:Mn^{2+}$	517	24	131	This work

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