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Electronic Supplementary Information

Luminescence center modulation towards a narrow-band green phosphor: mechanism and backlighting display application

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Experimental

***Material Synthesis*:** Mn^{2+} and Eu^{2+} co-doped $Sr_2MgAl_{22}O_{36}$ powders were synthesized with a solid-state synthesis method. The starting raw materials, $SrCO_3$ (A.R.), $Mg(OH)_2{\cdot}4MgCO_3{\cdot}5H_2O$ (A.R.), Al_2O_3 (A.R.), $MnCO_3$ (A.R.), Eu_2O_3(A.R.) and H_3BO_3 (A.R.) were thoroughly ground and mixed for 30 min with stoichiometric molar ratios in an agate mortar to form a homogeneous mixture. H_3BO_3 was used as flux and its amount was 5 wt% of the raw materials. Then the mixture was transferred into alumina crucibles and sintered at 1450 °C for 6 h under a reducing atmosphere of 90% N_2−10% H_2 in a horizontal tube furnace. After the furnace slowly cooled to room temperature, the calcined products were ground again, yielding the final phosphor powders.

***Characterization*:** The powder X-ray diffraction (XRD) data were recorded by an X-ray Diffractometer (Bruker D2 PHASER) with graphite monochromator using Cu Kα radiation (λ = 1.54056 Å) with the operating condition of 30 kV and 15 mA. Rietveld refinement was performed using the software GSAS.[1] The morphology of the sample was measured using scanning electron microscopy (SEM; Hitachi S-3600). The diffuse reflectance spectra (DRS) were recorded on a UV-vis spectro-photometer (PE-lambda950) by using the $BaSiO_4$ power as the reference. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were obtained by a spectro-fluorometer equipped with a 450W xenon lamp (Horiba Jobin Yvon, Fluorolog-3). The quantum efficiency of phosphor is measured using absolute PL quantum yield measurement system (Hamamatsu C9920-03 with monochromatic light source instruction manual). The fluorescence lifetime was measured by an Edinburgh FLS920 spectrometer. The performance of WLED device was tested on the UVS-near IR spectrophotocolorimeter (EVERFINE PHOTO-E-INFO Co., LTD., PMS-50/80). High temperature spectra measurements were performed using an aluminum plaque with cartridge heaters; the temperature was measured by thermocouples inside the plaque and controlled with a high temperature fluorescence controller (Orient KOJI instrument Co., Ltd., TAP-02).

***Computational Methodology*:** the electronic structures are calculated by employing the Vienna Ab initio Simulation Package (VASP)[2, 3] using the Perdew–Burke–Ernzerhof functional[4] under the general gradient approximation (GGA). The energy cutoff of the plane wave basis is set to 400 eV and the convergence criteria of energy to 10^{-4} eV. In the calculations, the Brillouin zones are sampled with a 2 × 2 × 2 k-points mesh of Monkhorst-Pack scheme. All the structures with doping are optimized with the criteria of that the force acted each of the atom is less than 0.03 eV/Å from initial structure

$Sr_2MgAl_{22}O_{36}$ reported in literatures. To consider the electron interaction accurately, the spin-polarized calculation is performed, and the Hubbard-U 4.0 eV and 7.0 eV for Mn *d*-electrons and Eu *f*-electrons atoms is chosen, respectively. In order to realize that the system does not have macroscopic magnetism, two magnetic atoms either for Mn or Eu are replaced at the same time, so that they form an anti-ferromagnetic structure, so that they form an anti-ferromagnetic structure. For the pseudopotential of rare-earth atom Eu, $[Kr4d]5s^25p^64f^76s^2$ configuration of is used in the calculations.

The formation energy of Mn doping (4.21 eV/atom) is calculated according to the following equation:

$$E(Mg_{Mn}) = \frac{E(Sr_{12}Mg_4Mn_2Al_{132}O_{216}) - 6 * E(Sr_2MgAl_{22}O_{36}) + 2 * E(Mg) - 2 * E(Mn)}{2}$$

The formation energy of Eu doping (0.76 eV/atom) is calculated according to the following equation:

$$E(Sr_{Eu}) = \frac{E(Sr_{10}Eu_2Mg_4Mn_2Al_{213}O_{216}) - E(Sr_{12}Mg_4Mn_2Al_{132}O_{216}) + E(SrO) - E(EuO)}{2}$$

Supplementary Figures and Tables

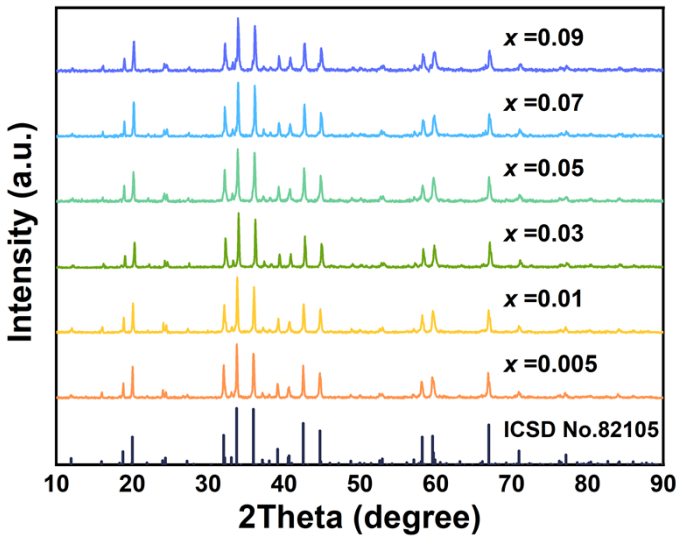

Figure S1. XRD pattern of the SMAO: xEu^{2+}, Mn^{2+}(0.5≤ x ≤9%) phosphors.

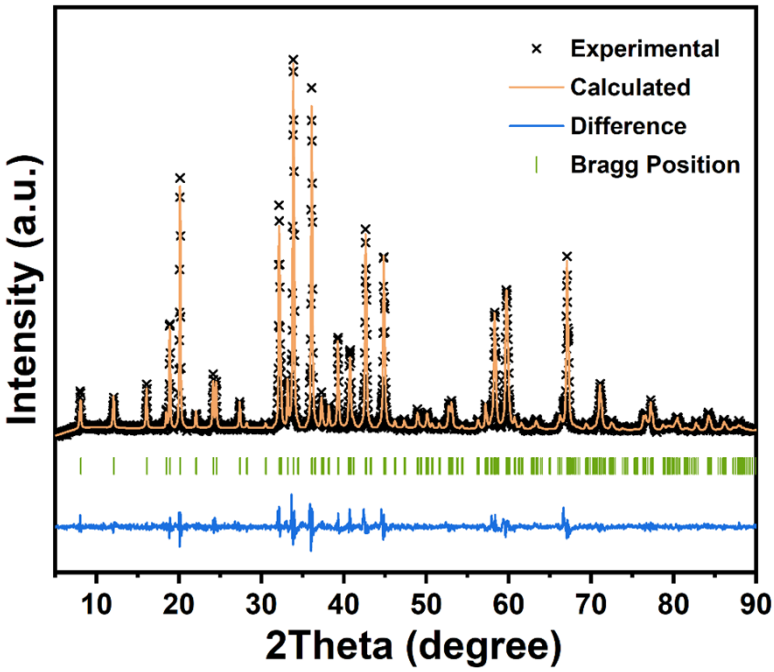

Figure S2. Representative Rietveld refinement XRD pattern of the SMAO host. The observed data, calculation data, and their difference are depicted with black crosses, red solid line, and blue solid line, respectively

Table S1 Structure parameters of the SMAO sample derived from XRD Rietveld refinements.

Formula	$Sr_2MgAl_{22}O_{36}$
Crystal system	Hexagonal
Space group	P-6m2
a/b (Å)	1.00
a (Å)	5.58(9)
c (Å)	22.23(6)
V (Å^3)	601.46(3)
R_p(%)	7.64
R_{wp}(%)	9.95

Table S2 Atomic parameters of the SMAO host.

Atom	Wyckoff position	x	y	z	Uiso.	Occ.
Sr1	1e	0.6667	0.3333	0	0.0235	1
Sr2	3k	0.30687	0.61373	0.5	0.0131	0.3201(3)
Al1	6n	0.82778	0.65555	0.14311	0.0227	1
Al2	6n	0.16425	0.32851	0.35699	0.0091	1
Al3	2h	0.3333	0.6667	0.213	0.0590	0.5
Mg1	2h	0.3333	0.6667	0.22116	0.0210	0.5
Al4	2i	0.6667	0.3333	0.27283	0.0078	1
Al5	2h	0.3333	0.6667	0.05958	0.0194	1
Al6	2i	0.6667	0.3333	0.42635	0.0160	1
Al7	2g	0	0	0.24871	0.0194	1
Al8	2g	0	0	0.01486	0.0071	0.5
O1	6n	0.14958	0.29917	0.19518	0.0136	1
O2	6n	0.84079	0.68159	0.29998	0.0351	1
O3	6n	0.50245	0.00491	0.10315	0.0521	1
O4	6n	0.49562	0.99124	0.39819	0.0007	1
O5	2i	0.6667	0.3333	0.18929	0.0040	1
O6	2h	0.3333	0.6667	0.30652	0.0276	1
O7	2g	0	0	0.10047	0.0304	1
O8	2g	0	0	0.39586	0.0035	1
O9	3j	0.18327	0.36653	0	0.0389	1
O10	3k	0.65115	0.30231	0.5	0.0479	0.333

Table S3 Structure parameters of the SMAO: 3%Eu^{2+}, 35%Mn^{2+} sample derived from XRD Rietveld refinements

Formula	$Sr_2MgAl_{22}O_{36}$: 3%Eu^{2+}, 35%Mn^{2+}
Crystal system	Hexagonal
Space group	P-6m2
a/b (Å)	1.00
a (Å)	5.59(5)
c (Å)	22.25(5)
V (Å^3)	603.29(4)
R_p(%)	8.78
R_{wp}(%)	6.58

Table S4 Atomic parameters of the SMAO: 3%Eu^{2+}, 35%Mn^{2+} sample.

Atom	Wyckoff position	x	y	z	Uiso.	Occ.
Sr1	1e	0.6667	0.3333	0	0.0312	1
Sr2	3k	0.2997	0.5994	0.5	0.0043	0.3384(7)
Al1	6n	0.82989	0.65978	0.1421	0.0264	1
Al2	6n	0.16613	0.33227	0.35698	0.0159	1
Al3	2h	0.3333	0.6667	0.21594	0.0659	0.5
Mg1	2h	0.3333	0.6667	0.2247	0.0030	0.325
Al4	2i	0.6667	0.3333	0.27497	0.0148	1
Al5	2h	0.3333	0.6667	0.05809	0.0278	1
Al6	2i	0.6667	0.3333	0.42502	0.0131	1
Al7	2g	0	0	0.25	0.0274	1
Al8	2g	0	0	0.01203	0.0000	0.5
O1	6n	0.14911	0.29822	0.19559	0.0174	1
O2	6n	0.83822	0.67644	0.30007	0.0328	1
O3	6n	0.50094	0.00189	0.10176	0.0429	1
O4	6n	0.49595	0.9919	0.39884	0.0047	1
O5	2i	0.6667	0.3333	0.18872	0.0045	1
O6	2h	0.3333	0.6667	0.30736	0.0265	1
O7	2g	0	0	0.10066	0.0162	1
O8	2g	0	0	0.39629	0.0123	1
O9	3j	0.18079	0.36157	0	0.0165	1
O10	3k	0.6468	0.29361	0.5	0.0003	0.333
Mn1	2h	0.3333	0.6667	0.21038	0.1138	0.175

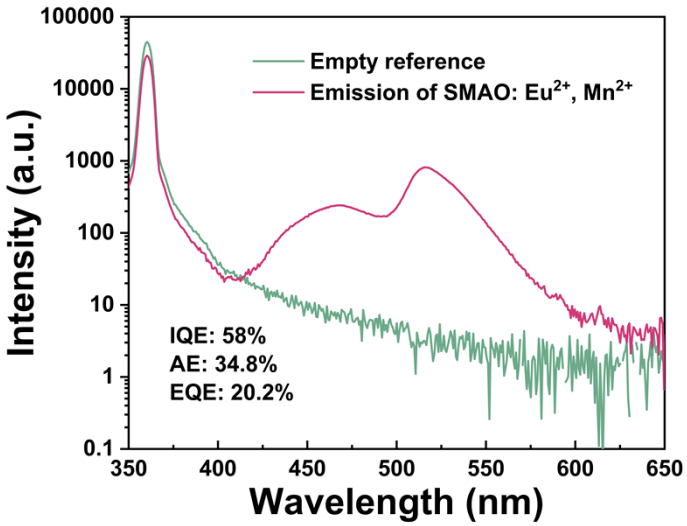

Figure S3. Quantum efficiency measurement of the SMAO: 3%Eu^{2+}, 35%Mn^{2+} sample.

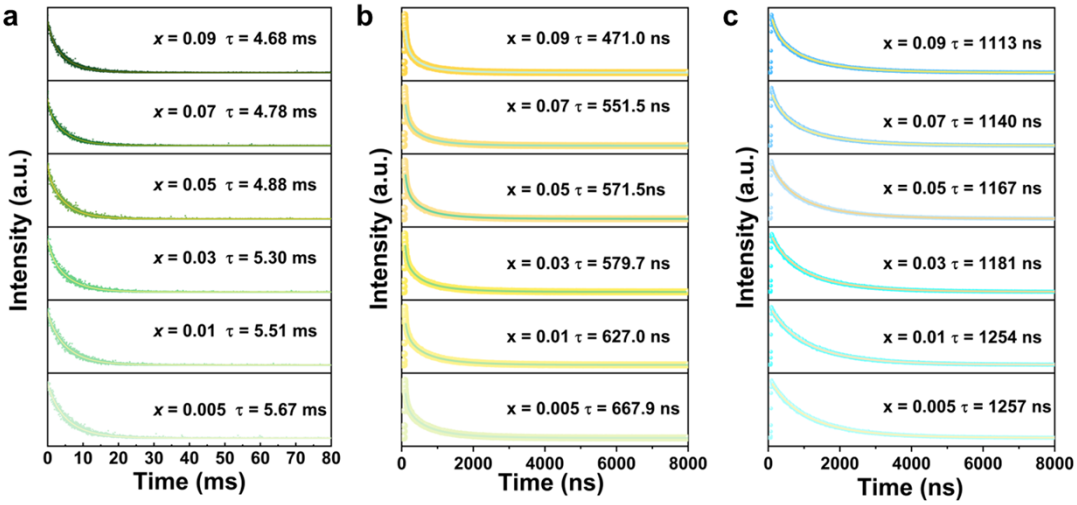

Figure S4. (a) Decay curves of Mn^{2+} emission for the SMAO:*x*Eu^{2+}, 35%Mn^{2+} (0.5≤ *x* ≤ 9%); (b) Decay curves of Eu^{2+} emission monitored at 465 nm for the SMAO:*x*Eu^{2+} (0.5≤ *x* ≤ 9%) and (c) SMAO:*x*Eu^{2+}, 35%Mn^{2+} (0.5≤ *x* ≤ 9%).

$$I(t) = A_0 + A_1\exp\left(-\frac{t}{\tau_1}\right) + A_2\exp\left(-\frac{t}{\tau_2}\right) \quad \text{(S1)}$$

where I (t) represent the luminescence intensity at time t, A_0 is the background luminescence intensity, A_1 and A_2 are constants; τ_1 and τ_2 are the decay times, respectively.

$$\eta_{ET} = 1 - (\frac{\tau}{\tau_0}) \quad \text{(S2)}$$

where τ and τ_0 are lifetimes of the Eu^{2+} emission with and without Mn^{2+}.

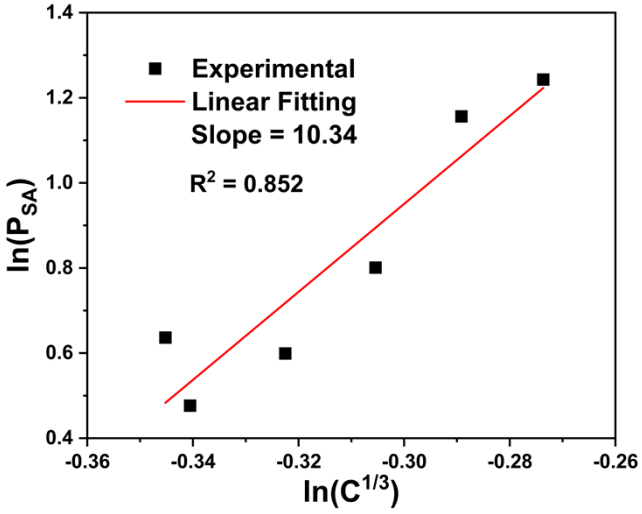

Figure S5. Plots of $\ln(P_{SA})$ vs $\ln(C^{1/3})$.

$$F(R)hv = C(hv - Eg)^{\frac{n}{2}} \quad \text{(S3)}$$

$$F(R) = \frac{(1-R^2)}{2R} \quad \text{(S4)}$$

where *R*, *h*, v, *C* and *Eg* present the reflection coefficient, Planck constant, light frequency, constant, optical band gap, respectively. The value of n is determined by the type of optical transition of a semiconductor (n = 1 for direct transition and n = 4 for indirect transition). Here, the value of n is 4.

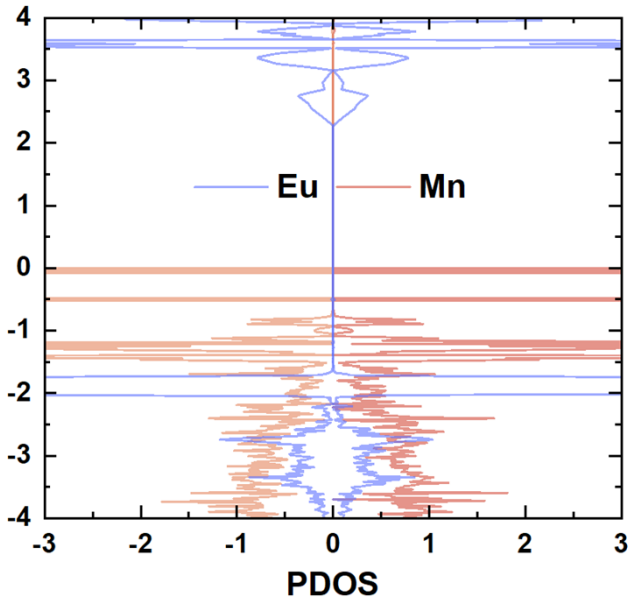

Figure S6. Partial density of state of Eu and Mn of SMAO: Eu^{2+}, Mn^{2+} phosphor

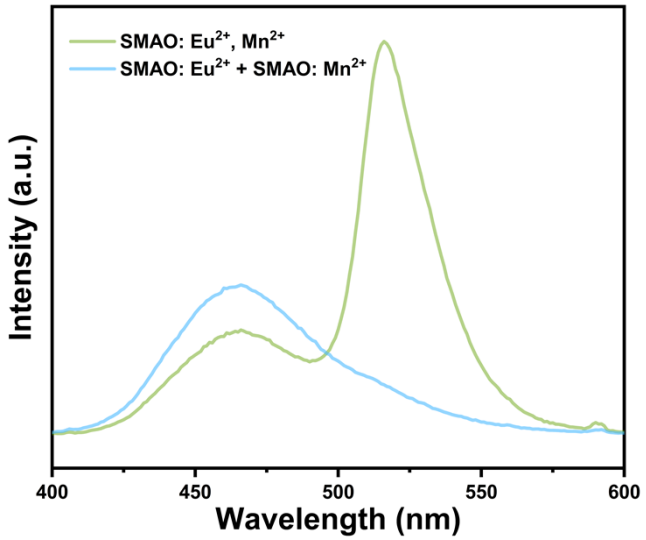

Figure S7. PL spectra of SMAO: 3%Eu^{2+}, 35%Mn^{2+} phosphor and the mixture of SMAO: 3%Eu^{2+} and SMAO: 35%Mn^{2+} phosphors.

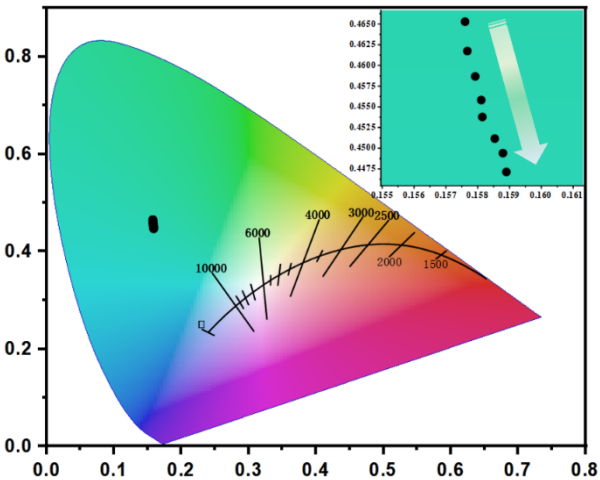

Figure S8. chroma excursion of the emission of SMAO: Eu^{2+}, Mn^{2+} phosphor dependent on temperature (25 °C-200 °C).

$$FWHM(T) = \sqrt{8 \cdot ln2} \times \sqrt{S} \times h\nu \times \sqrt{coth\frac{h\nu}{2kT}} \quad \text{(S5)}$$

where the FWHM (T) is derived from emission spectra at each temperature, hν is the phonon energy, and k is the Boltzmann's constant (8.617×10^{-5} eV/K).

Table S5 The luminescence parameters of SMAO: xEu^{2+}, 35%Mn^{2+} phosphors ($0.5 \leq x \leq 9\%$)

Eu^{2+} Concentration	Emission Peak(nm)		FWHM (nm)	Fluorescence lifetime		η(%)
	Eu^{2+}	Mn^{2+}		Eu^{2+}(ns)	Mn^{2+}(ms)	
0.005	466	517	28.351	677.9	5.67	46.1%
0.01	467	517	28.301	627.0	5.51	50.0%
0.03	468	517	28.365	579.7	5.30	50.9%
0.05	466	516	28.361	571.5	4.88	51.0%
0.07	467	517	28.376	551.5	4.78	51.6%
0.09	467	516	27.901	471.0	4.68	57.7%

Reference

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2. G. K. a. J. Furthmuller, *Phys. Rev. B*, 1996, 54, 11169-11186.
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