Electronic Supplementary Material (ESI) for Dalton Transactions.

Enhanced deep-red emission from Mn^{4+}/Mg^{2+} co-doped $CaGdAlO_4$ phosphors for plant cultivation

Jianxu Hu,[a,*] Tinghong Huang,[b,*] Yuanpeng Zhang,[c] Bin Lu,[a] Huanqing Ye,[d] Baojiu Chen,[e] Haiping Xia,[a] Changyan Ji,[f,*]

Supporting information

Contents

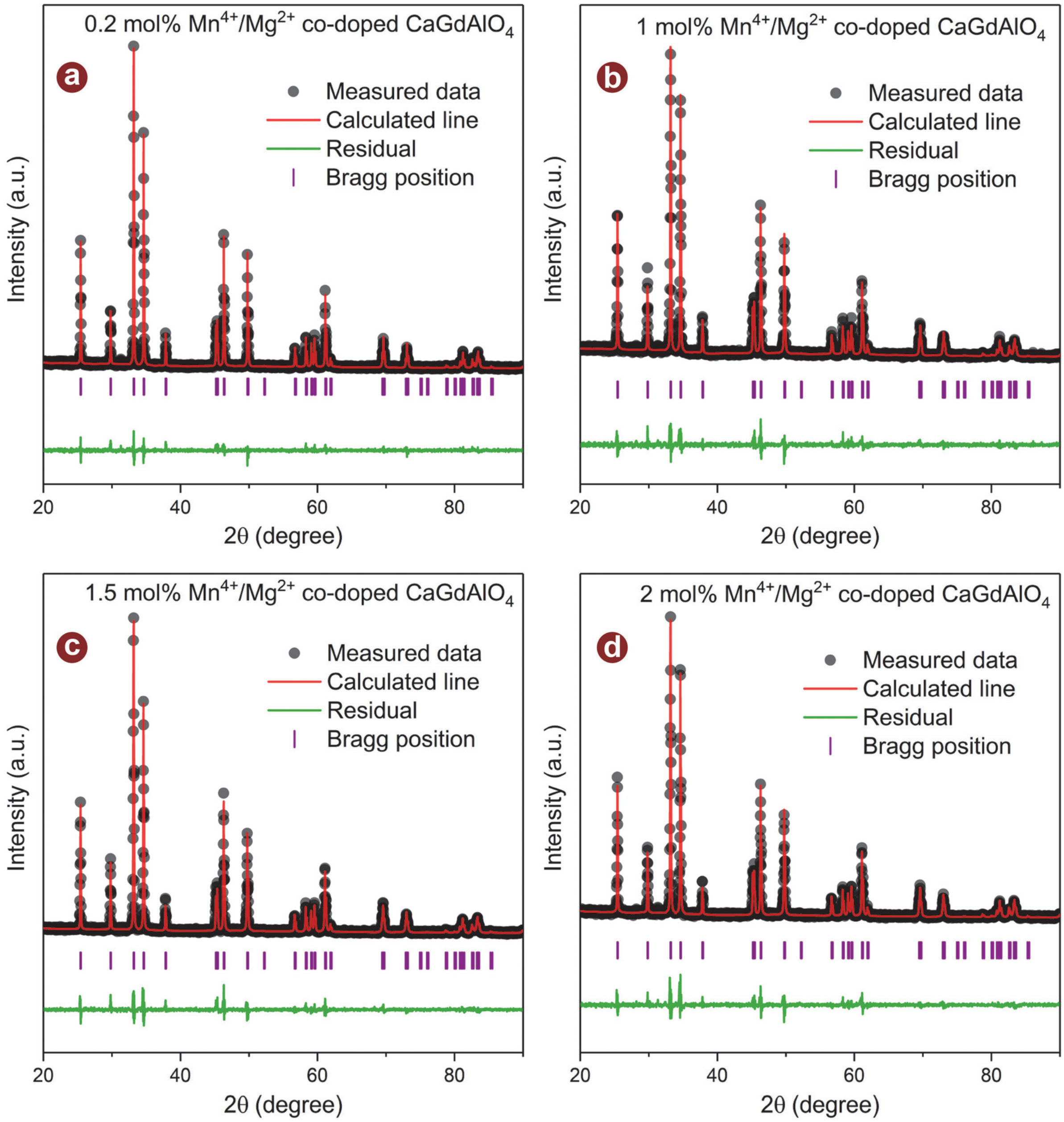

Fig. S1 (a)-(d) XRD Rietveld refinement results for *x* mol% Mn^{4+}/Mg^{2+} co-doped $CaGdAlO_4$ phosphors (x = 0.2, 1, 1.5, 2).

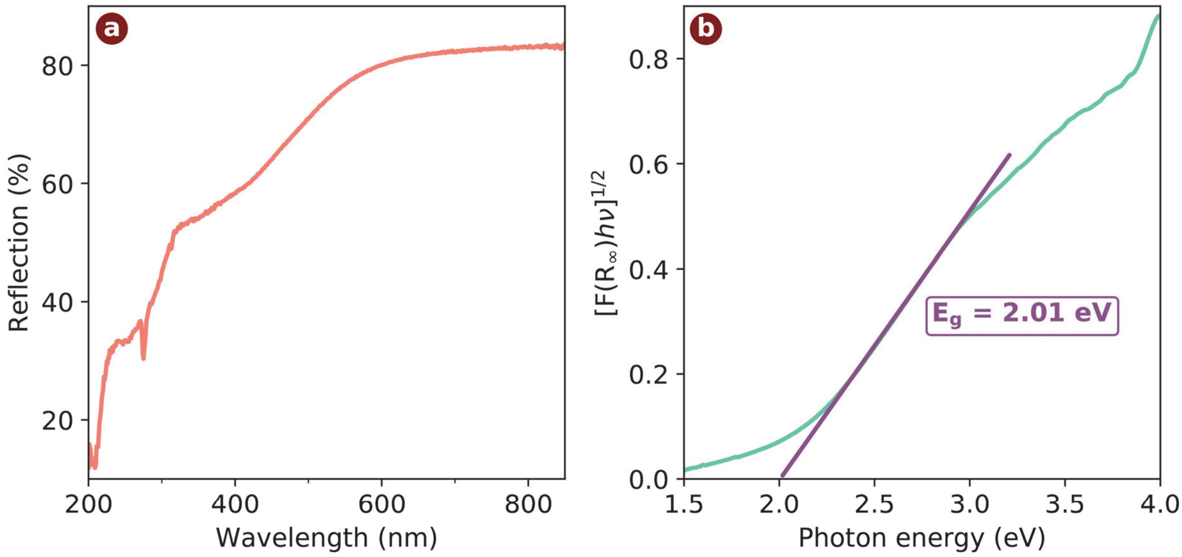

Fig. S2 (a) Diffuse reflection spectra of undoped CaGdAlO4 phosphor. (b) The dependence of $[F(R_\infty)h\upsilon]^{1/2}$ on the photon energy $h\upsilon$.

The energy gap (E_g) of CaGdAlO4 can be evaluated by the following equation:

$$[F(R_\infty)h\upsilon]^n = A(h\upsilon - E_g) \qquad (1)$$

where $h\upsilon$ denotes photon energy, A is a proportional constant, n equals to 1/2 for an indirect allowed transition. $F(R_\infty)$ is the Kubelka-Munk function, which can be expressed as:

$$[F(R_\infty)] = (1-R)^2/2R$$

where R is the reflection coefficient. $[F(R_\infty)h\upsilon]^{1/2}$ is plotted against $h\upsilon$ according to Taus method, from which the energy gap is determined to be 2.01 eV.

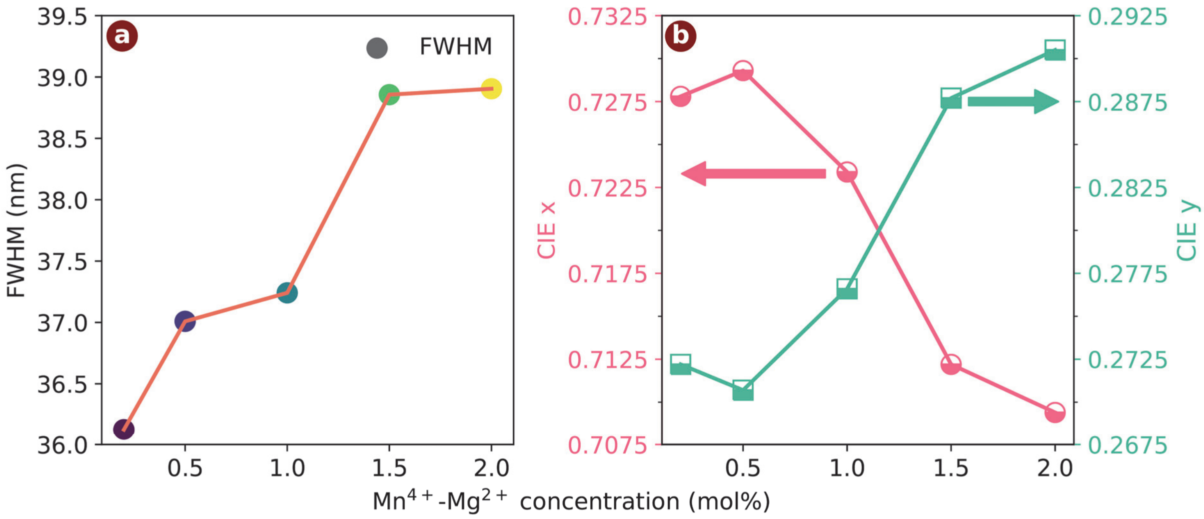

Fig. S3 (a) FWHM dependent plot on Mn^{4+}/Mg^{2+} doping concentration. (b) CIE chromaticity coordinates (x, y) as a function of Mn^{4+}/Mg^{2+} doping concentration.

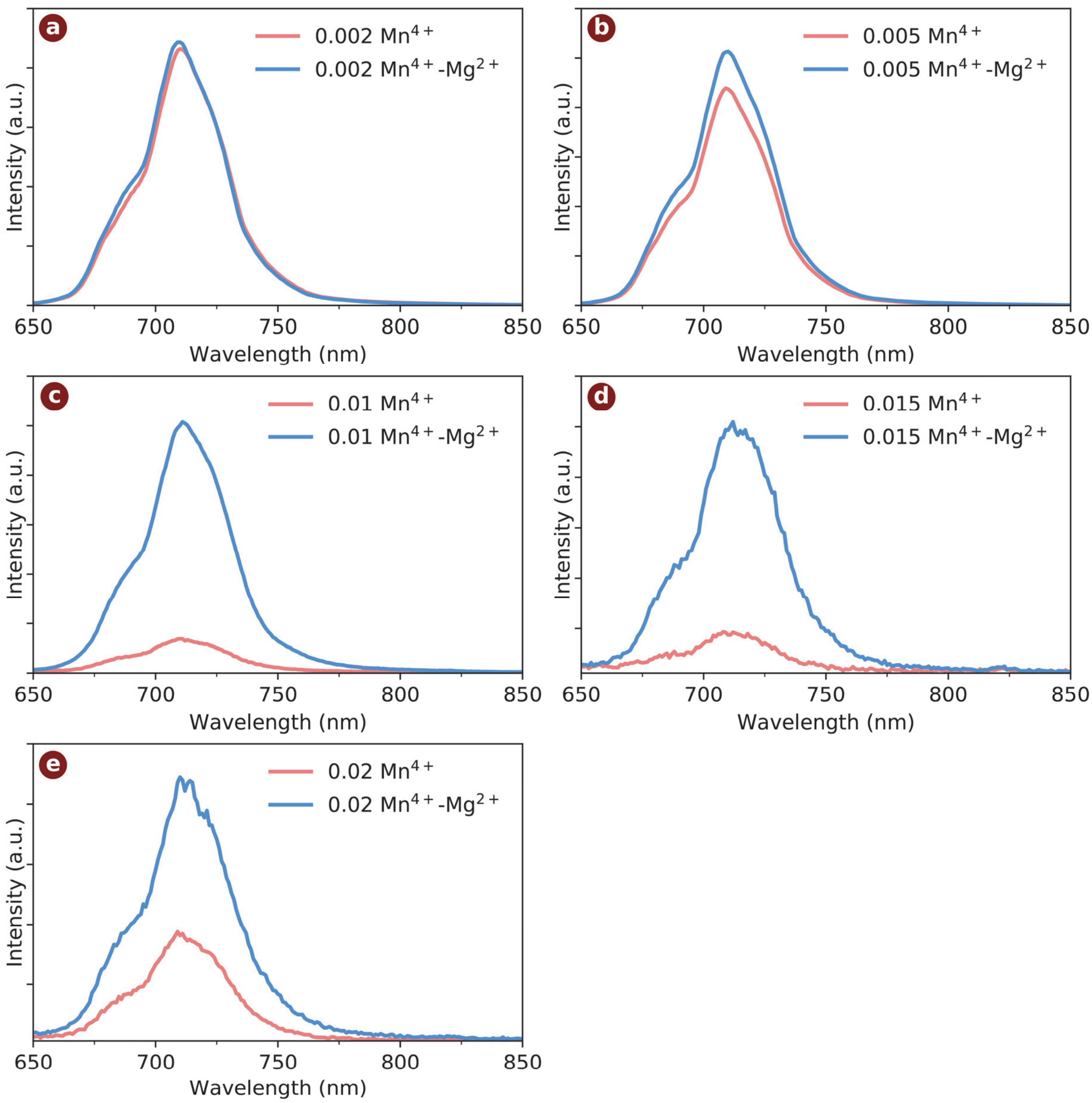

Fig. S4 (a)-(e) A comparison of red emission from Mn^{4+} ions with and without Mg^{2+} ions in $CaGdAlO_4$ host.

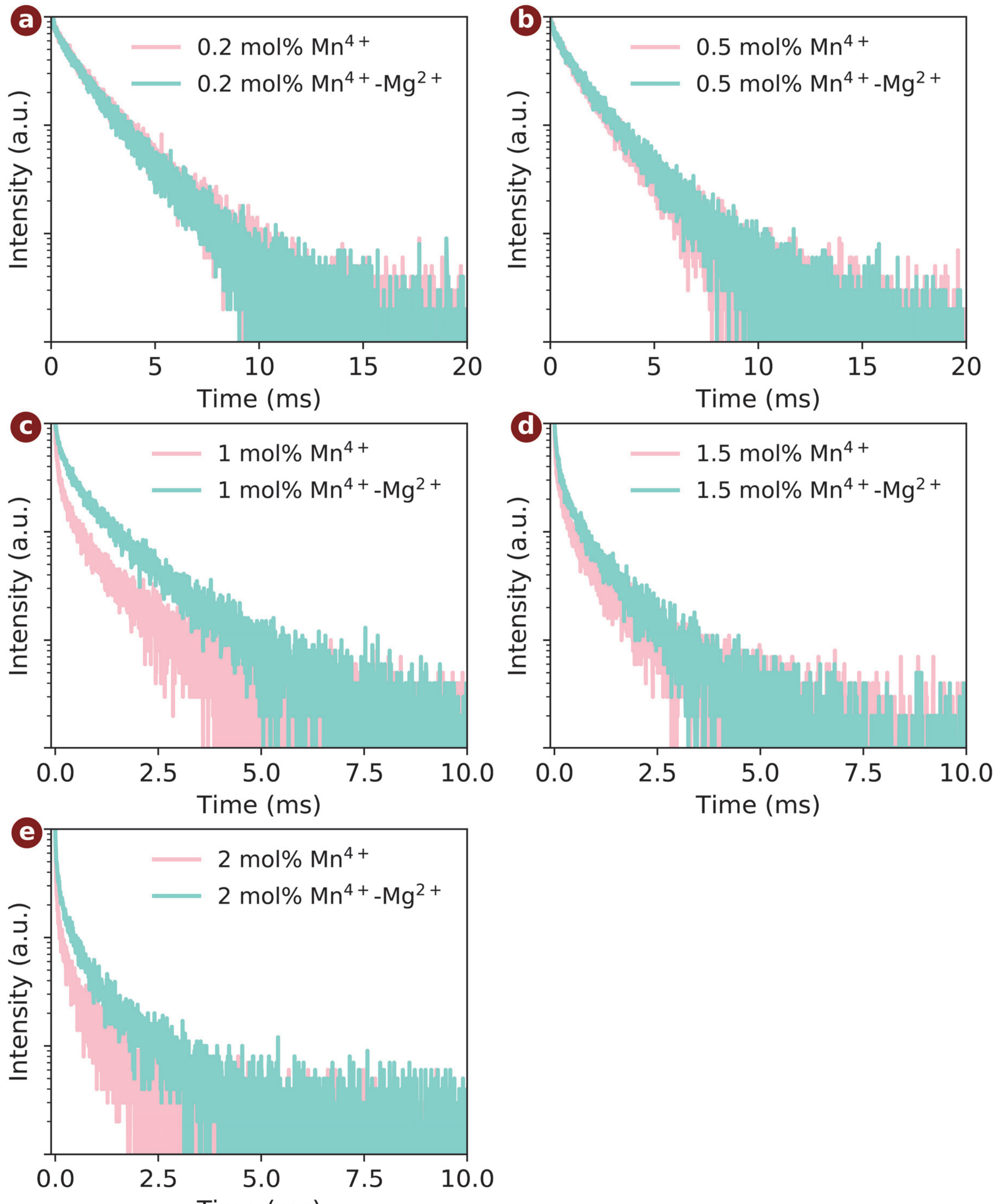

Fig. S5 (a)-(e) A comparison of decay time at 712 nm in the presence and absence of Mg^{2+} ions in $CaGdAlO_4$ host.

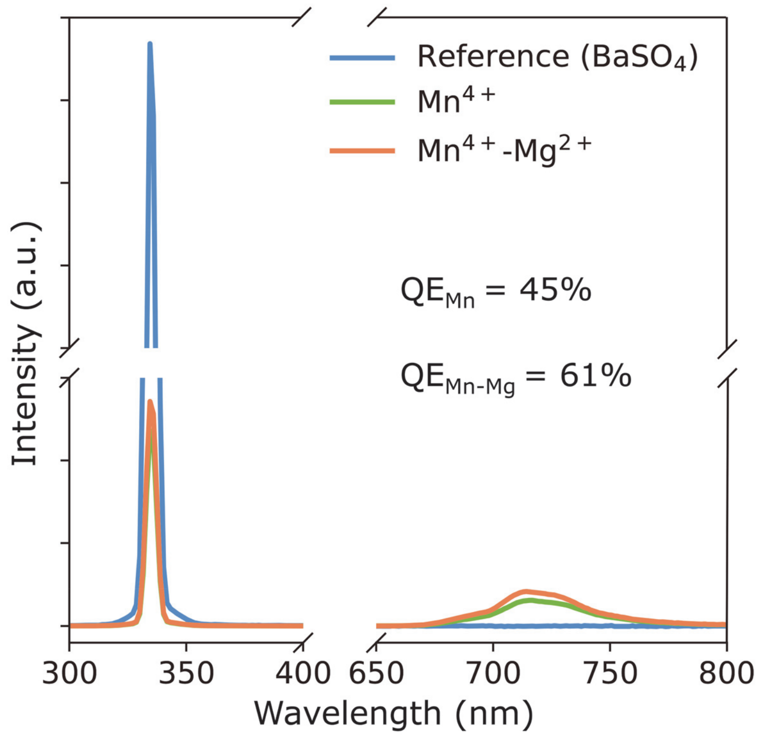

Fig. S6 Excitation spectra of $BaSO_4$ (in blue) and the emission spectra of 0.5 mol% Mn^{4+} singly doped (in green) and 0.5 mol% Mn^{4+}/Mg^{2+} co-doped (in red) phosphors under 335 nm excitation collected by an integrating sphere.

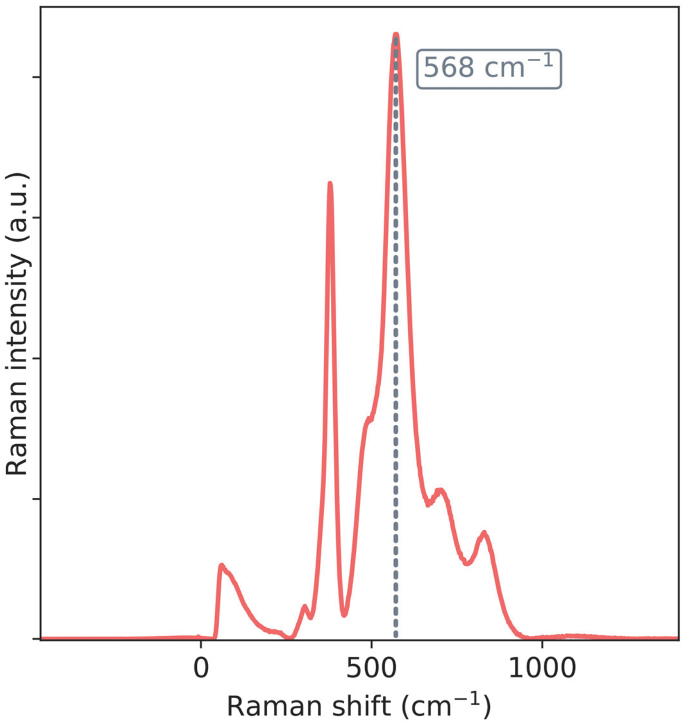

Fig. S7 Raman spectra of un-doped $CaGdAlO_4$ host.

Table S1 Crystallographic data of *x* mol% Mn^{4+}/Mg^{2+} co-doped $CaGdAlO_4$ phosphors (*x* = 0.2, 0.5, 1, 1.5, and 2) from Rietveld refinement.

Sample	0.2% Mn^{4+}/Mg^{2+}	0.5% Mn^{4+}/Mg^{2+}	1% Mn^{4+}/Mg^{2+}	1.5% Mn^{4+}/Mg^{2+}	2% Mn^{4+}/Mg^{2+}
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	*I4/mmm*	*I4/mmm*	*I4/mmm*	*I4/mmm*	*I4/mmm*
a (Å)	3.6613	3.6624	3.6637	3.6642	3.6657
b (Å)	3.6613	3.6624	3.6637	3.6642	3.6657
c (Å)	11.9890	11.9858	11.9857	11.9891	11.9916
V ($Å^3$)	160.71	160.76	160.88	160.97	161.13
α (deg)	90	90	90	90	90
β (deg)	90	90	90	90	90
γ (deg)	90	90	90	90	90
χ^2	2.85	2.51	2.03	2.27	2.33
R_p (%)	4.74	4.41	4.31	4.39	4.66
R_{wp} (%)	5.93	5.76	5.79	5.85	5.91

Table S2 Emission peaks and quantum efficiency for reported Mn^{4+} doped phosphors.

Phosphors	Peak wavelength (nm)	Quantum efficiency (%)	Reference
$La(MgTi)_{1/2}O_3$	708	27.2	12
Gd_2ZnTiO_6	705	39.7	54
$Ba_2TiGe_2O_8$	666	35.6	55
$Li_2Mg_3SnO_6$	670	36.3	56
La_2MgTiO_6	710	58.7	57
$NaMgLaTeO_6$	703	57.4	40
Sr_3NaSbO_6	695	56.2	58
Ca_2LaSbO_6	685	52.2	59
$BaLaMgNbO_6$	700	52.0	60
$CaGdAlO_4$	712	61.0	This work