Electronic Supplementary Information

Enhanced photoluminescence and phosphorescence properties of green phosphor $Zn_2GeO_4:Mn^{2+}$ via composition modification with GeO_2 and MgF_2

Yuexiao Pan, Li Li, Jing Lu, Ran Pang, Li Wang, Shaoming Huang

Table S1 The Mn^{2+} doped green phosphor samples prepared from ZnO, GeO_2, and MgF_2 with different molecule ratios sintered at 1100 ^oC for 5 h in air. (Note: $MnCO_3$ was used for source of Mn^{2+} doping with concentration of 1 mol% of Zn^{2+} for all the samples).

Sample names	Molecule ratios		
	ZnO	GeO_2	MgF_2
ZGOM	200	100	0
ZGOM-0.5GeO_2	200	150	0
ZGOM-1.0GeO_2	200	200	0
ZGOM-1.25GeO_2	200	225	0
ZGOM-1.5GeO_2	200	250	0
ZGOM-2.0GeO_2	200	300	0
ZGOM-1.0GeO_2-0.05MgF_2	200	200	5
ZGOM-1.0GeO_2-0.1MgF_2	200	200	10
ZGOM-1.0GeO_2-0.2MgF_2	200	200	20
ZGOM-1.0GeO_2-0.3MgF_2	200	200	30
ZGOM-1.0GeO_2-0.4MgF_2	200	200	40

Table S2 The Parameters for Crystallography and Refinement Crystallographic data.

	Crystallographic data	Atomic coordinates
GeO_2	R-Bragg 4.387 Space group P31-21 Wt% - Rietveld 34.55% Lattice parameters a 4.99749 (Å) c 5.65048 (Å)	Site x y z Ge1 0.44414(90) 0.00000 0.33333 O1 0.3786(27) 0.3019(19) 0.2207(32)
Zn_2GeO_4	R-Bragg 5.127 Spacegroup R-3 Wt% - Rietveld 65.45% Lattice parameters a 14.23500 (Å) c 9.52446 (Å)	Site x y z Ge1 0.2158(14) 0.1927(15) 0.2486(32) Zn1 0.2173(15) 0.1925(16) 0.5805(30) Zn2 0.2137(17) 0.1901(16) 0.9183(26) O1 0.1871(40) 0.1103(54) 0.0850(82) O2 0.1963(50) 0.1143(55) 0.4119(85) O3 0.2300(21) 0.1212(35) 0.7579(76) O4 0.3263(49) 0.3259(57) 0.2775(23)

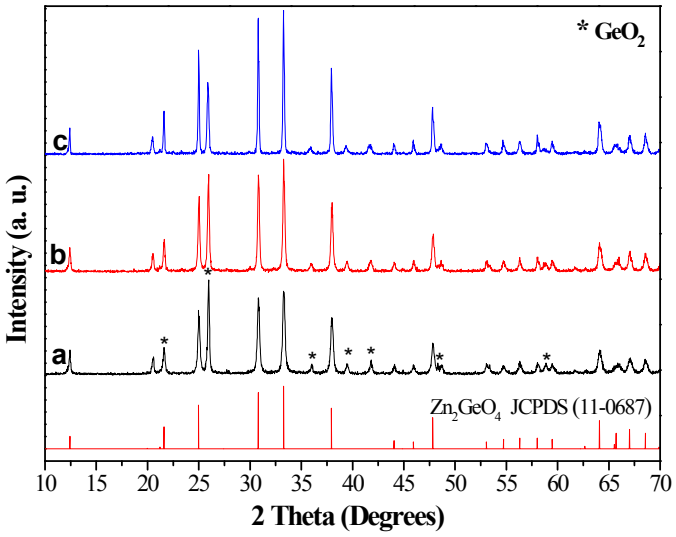

Figure S1 XRD patterns of Mn^{2+} doped samples prepared from starting materials ZnO, GeO_2 and $MnCO_3$ with molecule ratio of 99 ZnO:100 GeO_2: 1 $MnCO_3$ sintered

at (a) 700, (b) 900, and (c) 1100 °C for 5 h in air.

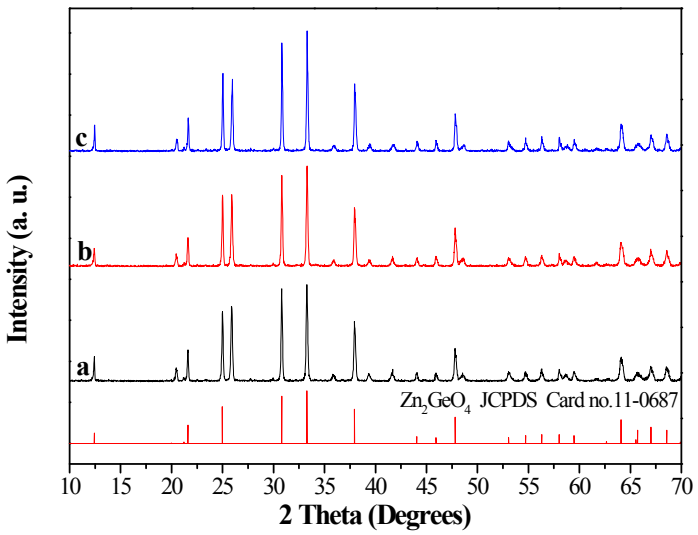

Figure S2 XRD patterns of Mn^{2+} doped samples prepared from ZnO and GeO_2 with molecule ratios of (a) 100 ZnO:100 GeO_2, (b) 110 ZnO:100 GeO_2 and (c) 120 ZnO:100 GeO_2 sintered at 1100 °C for 5 h in air.

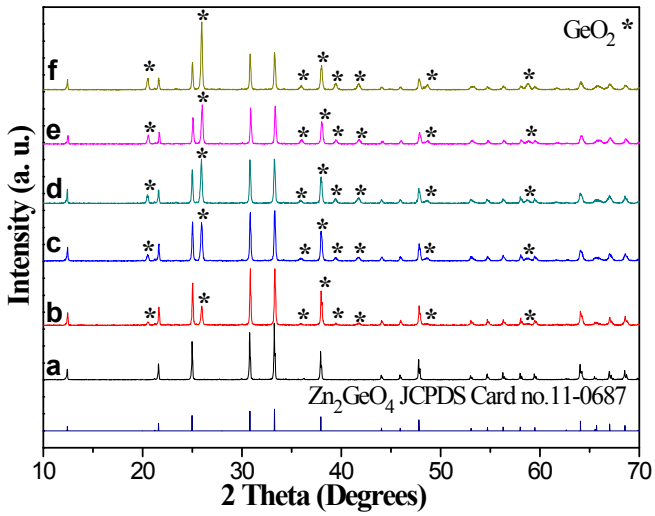

Figure S3 XRD patterns of Mn^{2+} doped phosphor samples: (a) ZGOM, (b) ZGOM-0.5GeO_2, (c) ZGOM-1.0GeO_2, (d) ZGOM-1.25GeO_2, (e) ZGOM-1.5GeO_2, and (f)

ZGOM-2.0GeO_2. (Note: "*" denotes GeO_2 phase.)

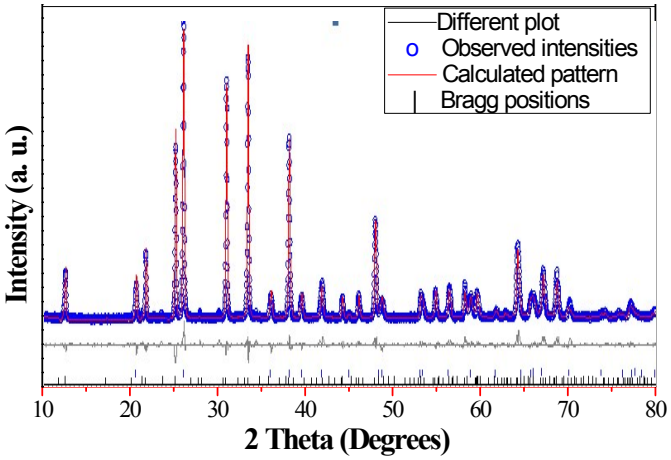

Figure S4 Rietveld refinement XRD patterns of the Mn^{2+} doped sample ZGOM-1.5GeO_2.

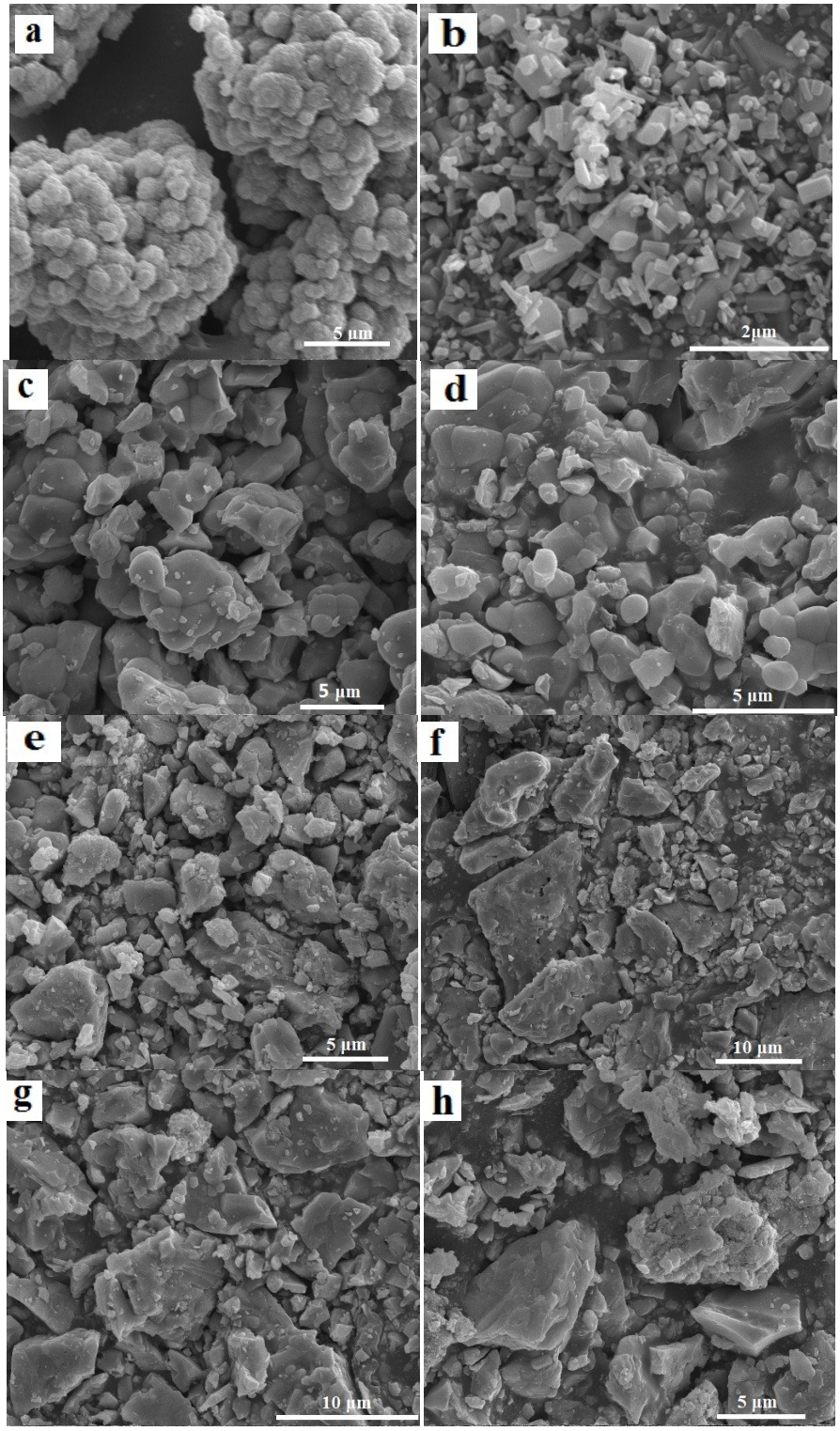

Figure S5 SEM images of starting materials (a) GeO_2 and (b) ZnO used in synthesis, and as-prepared samples (c) ZGOM, (d) ZGOM- 0.5 GeO_2, (e) ZGOM-1.0 GeO_2, (f)

ZGOM-1.25 GeO_2, (g) ZGOM-1.5 GeO_2, and (h) ZGOM- 2.0 GeO_2.

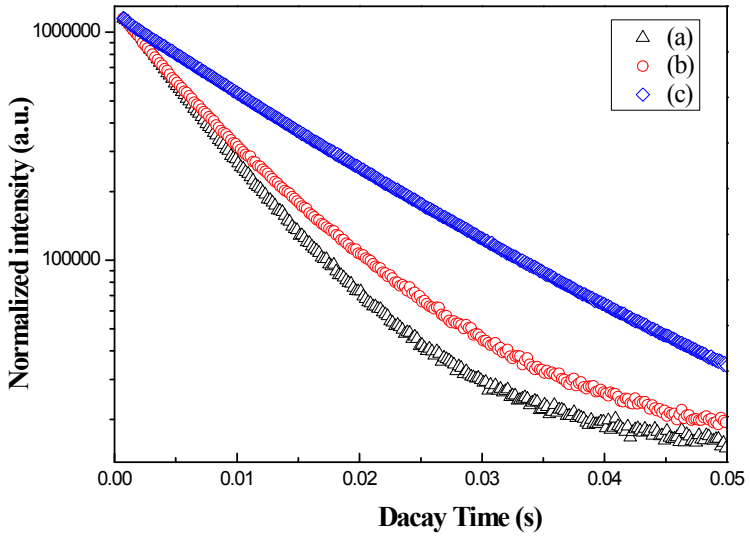

Figure S6 Decay curves of emission at 532 nm of samples: (a) ZGOM, (b) ZGOM-1.0GeO_2, (c) ZGOM-1.5GeO_2 excited at 350 nm measured at 77 K.

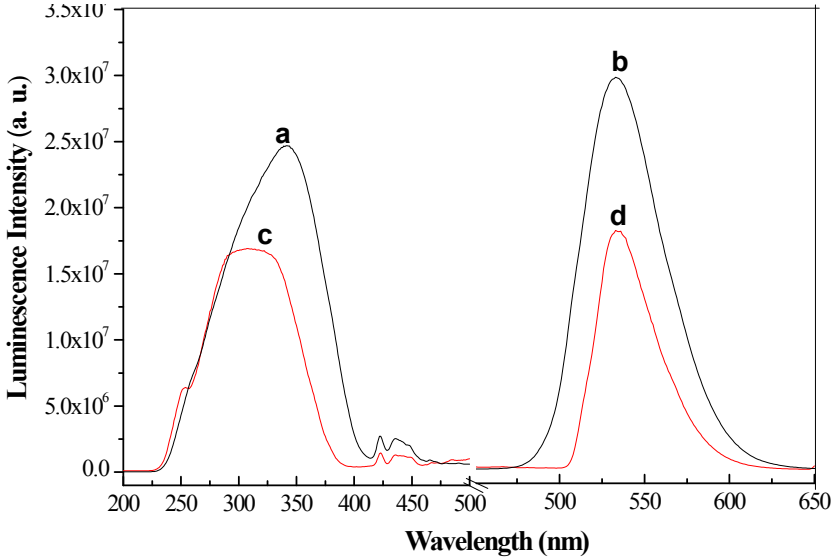

Figure S7 Excitation (λem = 532 nm) and emission (λex = 336 nm) spectra of Mn^{2+} doped sample ZGOM-1.5GeO_2 measured (a, b) at 298 K and (c, d) 77 K.

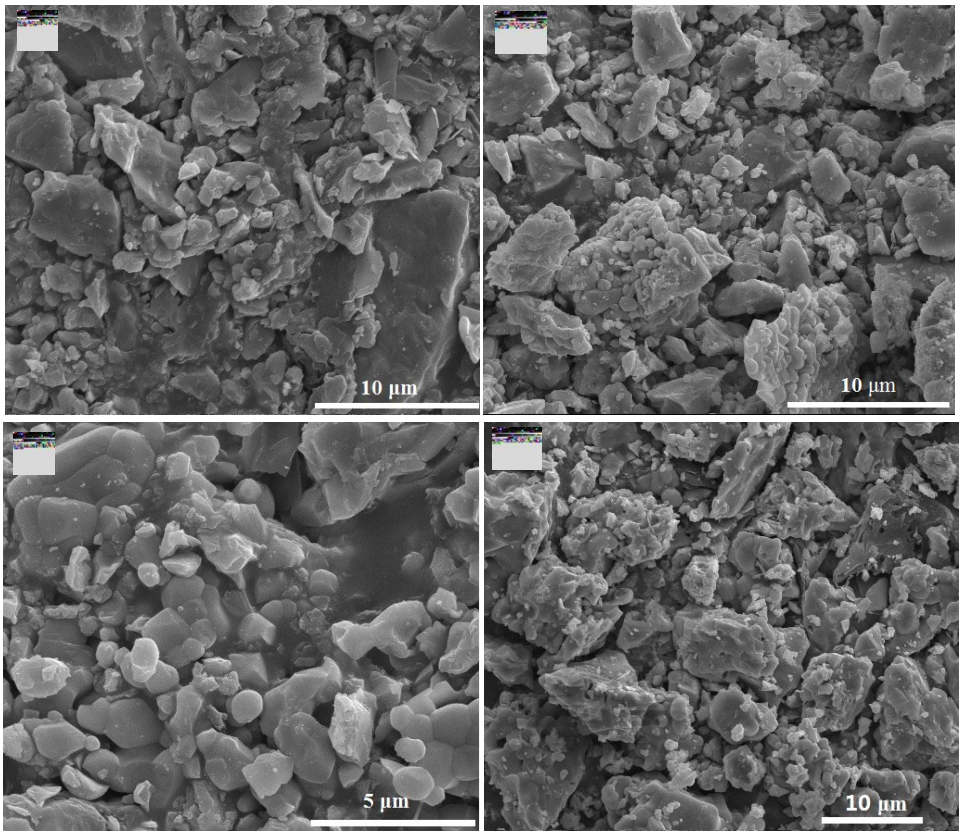

Figure S8 SEM images of as-prepared samples (a) ZGOM-1.0GeO_2-0.05MgF_2, (b) ZGOM-1.0GeO_2-1.0MgF_2, (c) ZGOM-1.0GeO_2-0.5MgF_2 and (d) ZGOM-1.0GeO_2-0.8MgF_2.

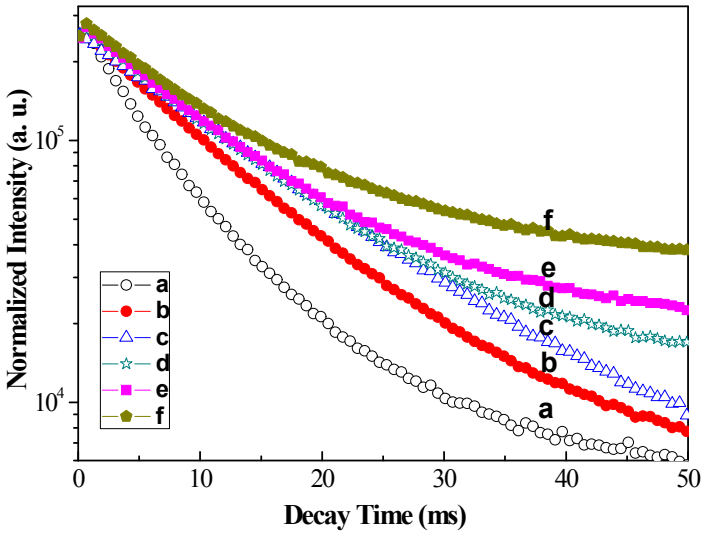

Figure S9 Decay curves of emission at 532 nm (excited at 350 nm) from samples: (a) ZGOM-1.0GeO_2, (b) ZGOM-1.0GeO_2-0.05MgF_2, (c) ZGOM-1.0GeO_2-0.1MgF_2, (d)

ZGOM-1.0GeO_2-0.2MgF_2, (e) ZGOM-1.0GeO_2-0.3MgF_2, and (f) ZGOM-1.0 GeO_2-0.4 MgF_2.

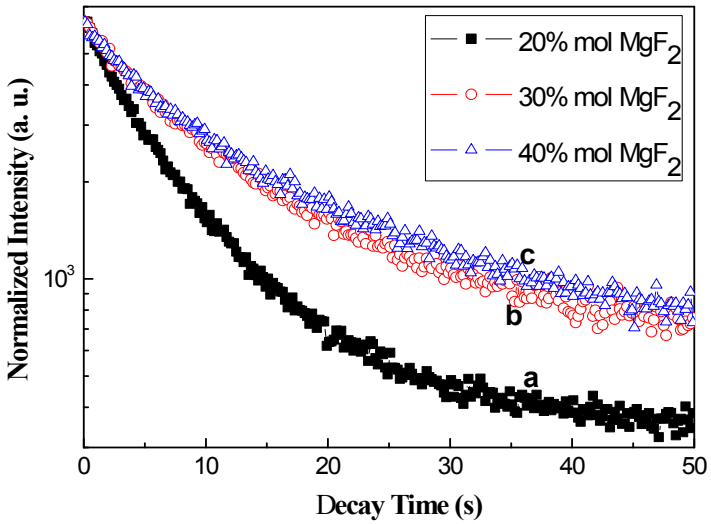

Figure S10 Decay curves of emission at 666 nm (excited at 350 nm) from samples (a) ZGOM-1.0GeO_2-0.2MgF_2, (b) ZGOM-1.0GeO_2-0.3MgF_2, and (c) ZGOM-1.0 GeO_2-0.4.

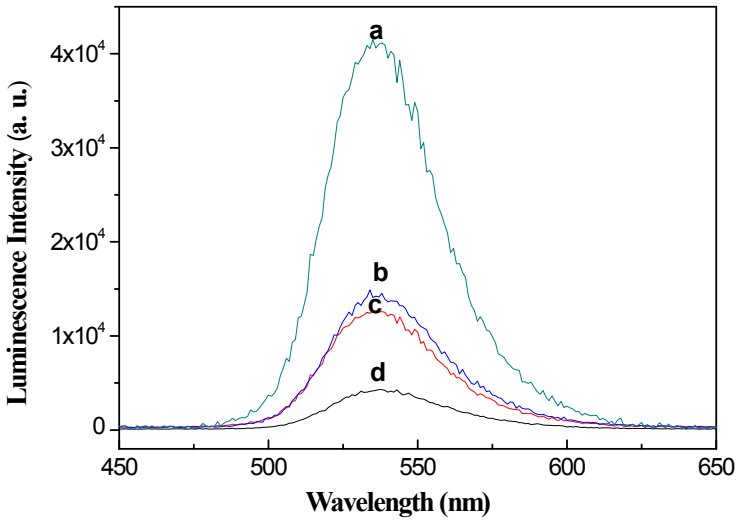

Figure S11 Long lasting emission spectra of sample ZGOM-1.5GeO_2 after the excitation source is switched off at (a) 5 min, (b) 10 min, (c) 15 min, (d) 30 min.

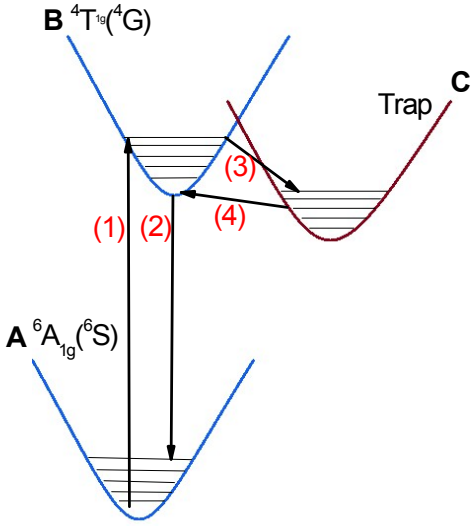

Figure S12 Configurational coordinate diagram of persistent luminescence of Mn^{2+} ions in Zn_2GeO_4.