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Supporting Information

Magical polyhedral twist *via* chemical unit co-substitution in $LaAlO_3:Mn^{4+}$ to greatly enhance the zero phonon line for high-efficiency plant-growth LEDs

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Experimental and characterization

Materials and synthesis

A series of near-infrared $LaAl_{0.999-x}(Mg/Ge)_xO_3:0.001Mn^{4+}$ (LAMG:Mn^{4+}, x=0-0.5) phosphors were synthesized by the high-temperature solid-state reaction. La_2O_3, Al_2O_3, $MgCO_3$, GeO_2 and $MnCO_3$ were employed as raw materials. Rare-earth oxides La_2O_3 is 99.99 % pure product purchased from Huizhou Ruier Rare-Chem. Hi-Tech. Co. Ltd (Huizhou, China). Al_2O_3 (99.99%), GeO_2 (99.99%) and $MnCO_3$ (99.95%) were purchased from Aladdin Chemical Reagent Co. Ltd (Shanghai, China). $MgCO_3$ (99.99%) was purchased from Xiya Reagent Co. Ltd (Shandong, China). La_2O_3 was calcined at 1000 ^oC for 2 h to remove adsorbed water before using, while other powers were used directly without any purification. According to the composition, the above materials were weighted stoichiometrically. After that, the mixtures were transferred into an agate mortar and grounded thoroughly for 30 min, pre-fired at 1000 °C for 5 h and subsequently sintered at 1500 °C for 8 h in air. Finally, after cooling down to room temperature, the LAMG:Mn^{4+} phosphors were collected for further analysis.

LEDs fabrication

The LED lighting devices were fabricated by combining the 365 nm UV chip with phosphors. The typical fabrication process was as follows: First, the appropriate amounts of phosphors were added into the mixture of type A and B epoxy resin, and all the materials were mixed uniformly. After blending thoroughly, the obtained mixture was coated on the surface of chips uniformly. Then, the chips were transferred in oven under heating at 60 °C for 40 min to remove bubbles and 135 °C for 2 h to solidify epoxy resin completely. Finally, after cooling down to the room

temperature, the LED devices were prepared for further measurements.

Characterization

Phase identification was performed by X-ray diffraction (XRD, Model SmartLab, Rigaku, Tokyo, Japan), operating at 40 kV/200 mA using nickel-filtered Cu Kα radiation (λ=0.15406 nm) and a scanning speed of 6.0° 2θ/min from 10° to 90°. The XRD data for Rietveld refinement was obtained in a step-scan mode, using a step interval of 0.02° and a counting time of 2.5 s per step over the 2θ range from 10° to 110°. The sample morphology was analyzed by transmission electron microscopy (TEM, Model JEM-2000FX, JEOL, Tokyo). Diffuse reflectance spectra of the samples were taken on a UV-Vis-NIR spectrophotometer (UV-3600 Plus, Shimadzu, Kyoto, Japan) at room temperature. The Raman scattering measurements were carried out using the Raman microscope (Model R-XploRA Plus, Horiba, Kyoto) with a 638 nm laser as the excitation source. Electron paramagnetic resonance (EPR) spectra were carried out using a EPR spectrometer (JES-FA 200, JEOL, Kyoto), and the frequency was 9.063 GHz. Photoluminescence and fluorescence decay of the LAMG:Mn^{4+} phosphors were analyzed by an FP-8600 fluorospectrophotometer (JASCO, Tokyo) equipped with a 150 W Xe-lamp for excitation and an accessory for temperature-control (HPC-836, JASCO), using a scan speed of 500 nm/min and slit width of 10 nm for both excitation and emission. Luminescence signal of the LED lamp fabricated by combining the phosphor with a 365 nm NUV LED chip was collected with a Model HS-1000 spectral detector (Otsuka Electronics Co. Ltd., Osaka, Japan).

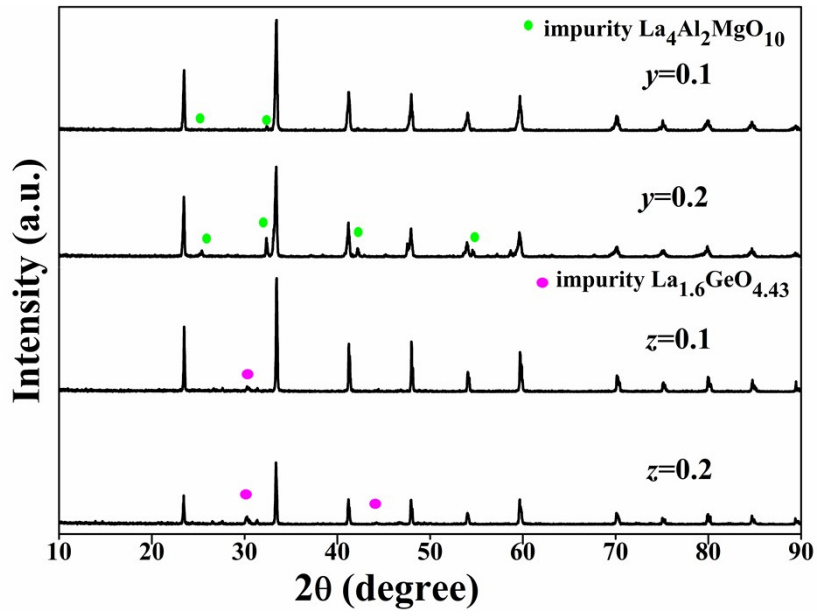

Fig. S1 XRD patterns of $LaAl_{1-y}Mg_yO_3$:0.001Mn^{4+} (y=0.1, 0.2) and $LaAl_{1-z}Ge_zO_3$:0.001Mn^{4+} (z=0.1, 0.2) phosphors.

Table S1 Wyckoff lattice position (Wyck), atomic coordinates (*x*, *y*, *z*), isotropic displacement parameter (B_{iso}) and atom occupancy (Occ.) for $LaAlO_3$ and LAMG:Mn^{4+} (*x*=0-0.4)

Atom	Wyck.	*x*	*y*	*z*	B_{iso} (Å^2)	Occ.
$LaAlO_3$ host						
La	1a	0	0	0	1.017(49)	1
Al	1a	0.5	0.5	0.5	0.87(15)	1
O	3b	0.5	0.5	0	0.81(17)	1
$LaAl_{0.999}O_3$:0.001Mn^{4+}						
La	1a	0	0	0	0.149(26)	1
Al	1a	0.5	0.5	0.5	0.090(74)	0.999
O	3b	0.5	0.5	0	0.586(87)	1
Mn	1a	0.5	0.5	0.5	0.090(74)	0.001
$LaAl_{0.899}(Mg/Ge)_{0.1}O_3$:0.001$Mn^{4+}$						
La	1a	0	0	0	1.246(40)	1
Al	1a	0.5	0.5	0.5	0.91(11)	0.899
O	3b	0.5	0.5	0	2.64(17)	1
Mg	1a	0.5	0.5	0.5	0.91(11)	0.05
Ge	1a	0.5	0.5	0.5	0.91(11)	0.05
Mn	1a	0.5	0.5	0.5	0.91 (11)	0.001
$LaAl_{0.799}(Mg/Ge)_{0.2}O_3$:0.001$Mn^{4+}$						
La	1a	0	0	0	0.863(61)	1
Al	1a	0.5	0.5	0.5	1.40(21)	0.799
O	3b	0.5	0.5	0	3.00(25)	1
Mg	1a	0.5	0.5	0.5	1.40(21)	0.1
Ge	1a	0.5	0.5	0.5	1.40(21)	0.1
Mn	1a	0.5	0.5	0.5	1.40(21)	0.001
$LaAl_{0.699}(Mg/Ge)_{0.3}O_3$:0.001$Mn^{4+}$						
La	1a	0	0	0	0.010(43)	1
Al	1a	0.5	0.5	0.5	0.82(15)	0.699

O	3b	0.5	0.5	0	2.49(23)	1
Mg	1a	0.5	0.5	0.5	0.82(15)	0.15
Ge	1a	0.5	0.5	0.5	0.82(15)	0.15
Mn	1a	0.5	0.5	0.5	0.82(15)	0.001
$LaAl_{0.599}(Mg/Ge)_{0.4}O_3:0.001Mn^{4+}$						
La	1a	0	0	0	1.015(78)	1
Al	1a	0.5	0.5	0.5	2.07(21)	0.599
O	3b	0.5	0.5	0	1.51(28)	1
Mg	1a	0.5	0.5	0.5	2.07(21)	0.2
Ge	1a	0.5	0.5	0.5	2.07(21)	0.2
Mn	1a	0.5	0.5	0.5	2.07(21)	0.001

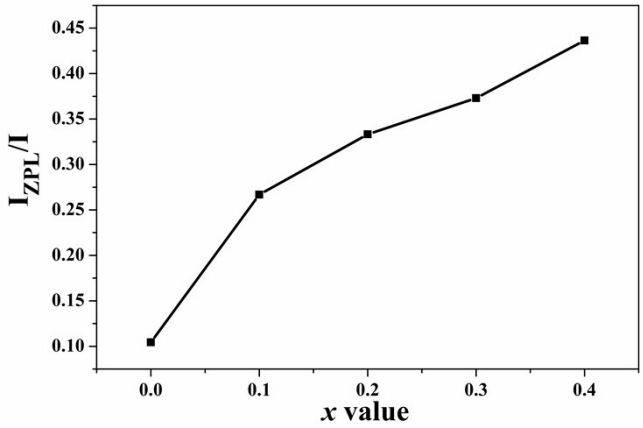

Fig. S2 Related intensity ratio between ZPL and total emission.

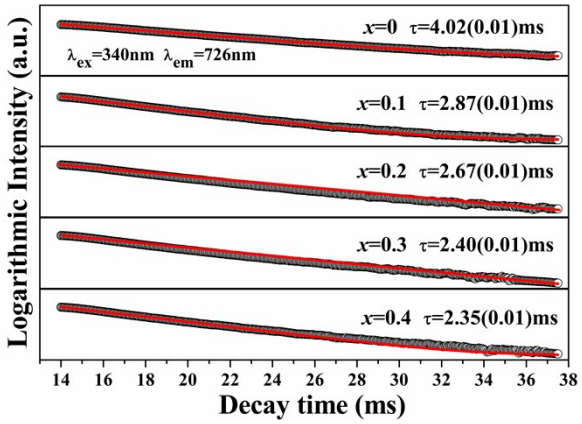

Fig. S3 Decay curves of LAMG:Mn^{4+} (x=0-0.4) under excitation at 340 nm and monitoring at 726 nm at room temperature.

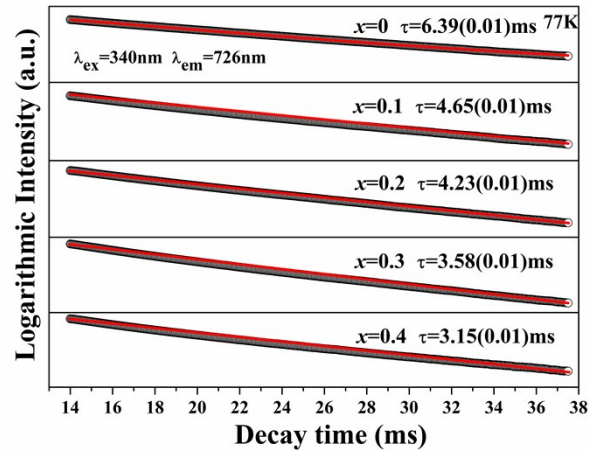

Fig. S4 Decay curves of LAMG:Mn^{4+} (x=0-0.4) under excitation at 340 nm and monitoring at 726 nm at 77 K.

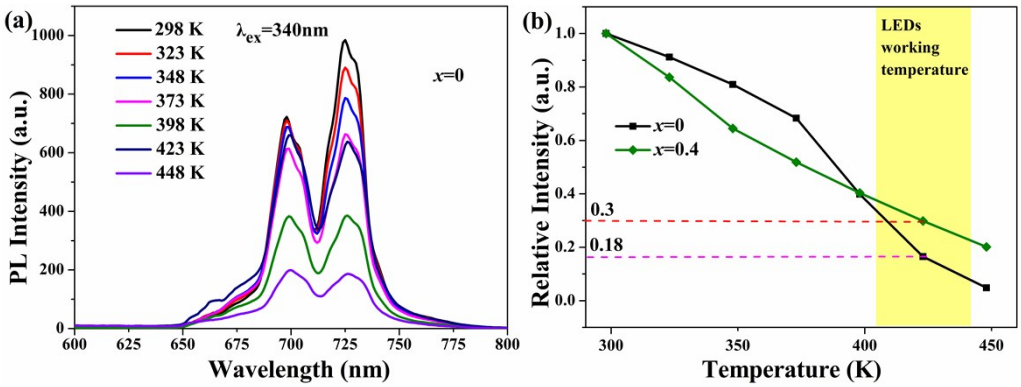

Fig. S5 (a) Temperature dependence of PL spectra for x=0 sample. (b) is the temperature dependence of integrated emission intensity of x=0 and 0.4 samples.

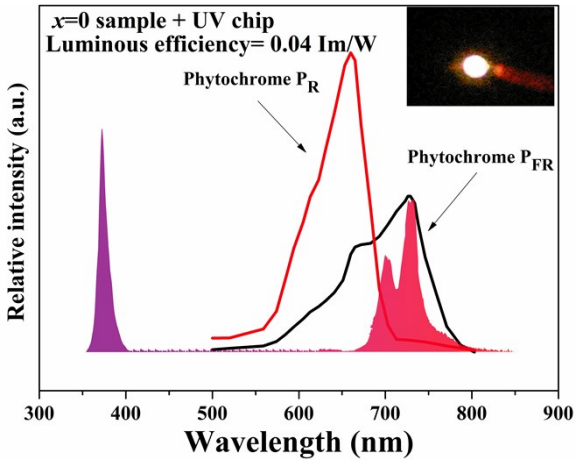

Fig. S6 Electroluminescence emission spectra of the fabricated LEDs with x=0 sample on the 365 nm UV chip. The inset shows the image of the fabricated LED under 100 mA drive current.