

Cyan-Emitting Ti^{4+} - and Mn^{2+} -Coactivated Mg_2SnO_4 as a Potential Phosphor to Enlarge Color Gamut for Field Emission Display

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Experimental Section:

Preparation. The Mg_2SnO_4 : x mol% Ti^{4+} , y mol% Mn^{2+} powder samples were prepared by conventional solid state reaction. The doping concentrations of Ti^{4+} and Mn^{2+} were chosen as 0.1–5 mol% of Sn^{4+} and 0.01–1 mol% of Mn^{2+} in Mg_2SnO_4 , respectively. Typically, stoichiometric amounts of MgO , SnO_2 , TiO_2 , and MnCO_3 were thoroughly mixed with an appropriate amount of ethanol in an agate mortar and then dried at 90 °C for 2 h. The powder mixtures were sintered at 1200 °C for 4 h in air to produce the final samples. All chemicals are of analytical degree.

Characterization. The X-ray diffraction (XRD) measurements were carried out on a D8 Focus diffractometer using Cu K α radiation ($\lambda = 0.15405$ nm). The PL measurements were performed on a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The CL measurements were carried out in an ultra-highvacuum chamber ($<10^{-8}$ Torr), where the phosphors were excited by an electron beam in the voltage range of 0.5–5.0 kV and different anode current density, and the emission spectra were recorded using an F-7000 spectrophotometer. Photoluminescence quantum yield (QY) was measured by absolute PL quantum yield measurement system C9920-02. The PL lifetimes of the samples were measured with a Lecroy Wave Runner 6100 Digital Oscilloscope (1GHz) using a tunable laser (pulse width 4 ns) as the excitation source (Continuum Sunlite OPO). All the measurements were performed at room temperature (RT).

Table 1. Ionic radii (\AA) and their coordination number (CN) of Mg^{2+} , Mn^{2+} , Sn^{4+} and Ti^{4+} .

Ion	CN = 4		CN = 6	
	Crystal radius (CR) (\AA)	Effective ionic radius (IR) (\AA)	Crystal radius (CR) (\AA)	Effective ionic radius (IR) (\AA)
Mg^{2+}	0.71	0.57	0.86	0.72
Mn^{2+}	0.80	0.66	0.81	0.67
Sn^{4+}	—	—	0.83	0.69
Ti^{4+}	—	—	0.745	0.605

Table 2. The CIE chromaticity coordinates, emission colors of $\text{Mg}_{2(1-y)}\text{Sn}_{(1-x)}\text{O}_4$: x mol% Ti^{4+} , y mol% Mn^{2+} (x = 0-3, y = 0-0.1) samples under the $V_a = 3.0 \text{ kV}$, $J_a = 50 \mu\text{A}/\text{cm}^2$ electron beam excitation, and their quantum yields under $\lambda_{ex} = 244 \text{ nm}$ UV light excitation.

Sample	$\text{Mg}_{2(1-y)}\text{Sn}_{(1-x)}\text{O}_4$: x mol% Ti^{4+} , y mol% Mn^{2+}	Quantum yield (%)	CIE chromaticity coordinates (X, Y)	Color
S1	x = 0, y = 0	—	(0.1780, 0.2449)	blue
S2	x = 2.0, y = 0	35	(0.1773, 0.2186)	blue
S3	x = 0, y = 0.1	4	(0.0908, 0.5668)	green
S4	x = 0.5, y = 0.01	17	(0.1512, 0.2717)	cyan
S5	x = 0.5, y = 0.025	18	(0.1464, 0.2871)	cyan
S6	x = 0.5, y = 0.05	13	(0.1409, 0.3185)	cyan
S7	x = 2.0, y = 0.01	23	(0.1637, 0.2574)	cyan
S8	x = 2.0, y = 0.025	22	(0.1647, 0.2819)	cyan
S9	x = 3.0, y = 0.01	19	(0.1676, 0.2397)	cyan

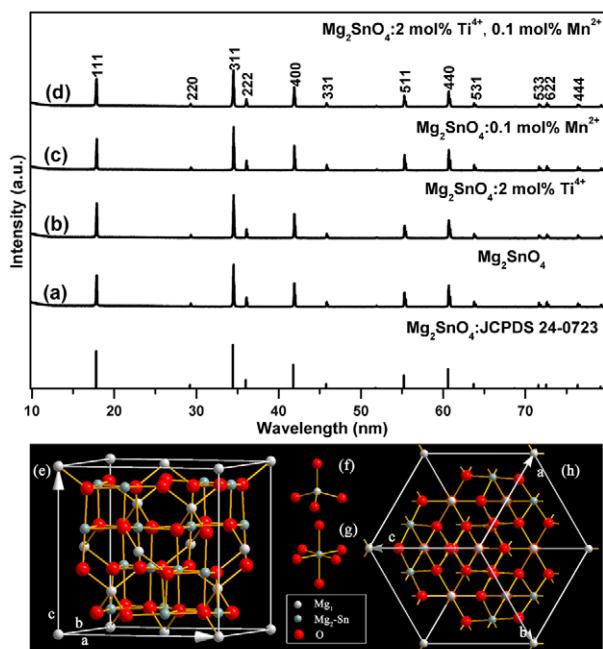


Fig. S1 The XRD patterns of (a) Mg₂SnO₄, (b) Mg₂SnO₄:2 mol% Ti⁴⁺, (c) Mg₂SnO₄:0.1 mol% Mn²⁺, (d) Mg₂SnO₄:2 mol% Ti⁴⁺, 0.1 mol% Mn²⁺ samples calcined at 1200 °C for 4 h and the standard data for Mg₂SnO₄ (JCPDS No. 24-0723) as reference. (e)-(h) are the schematic drawing of the crystal structure of Mg₂SnO₄.

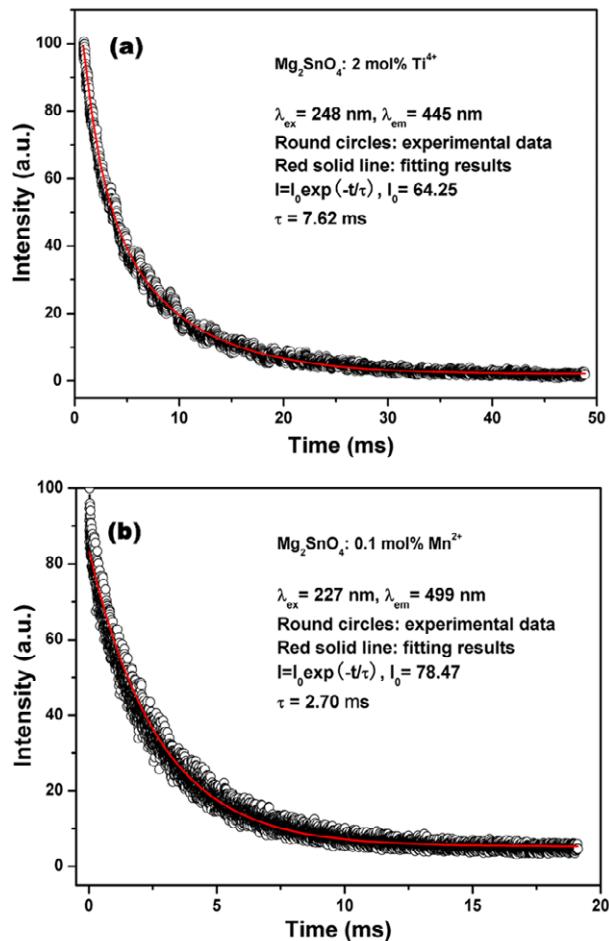


Fig. S2 The photoluminescence lifetime of Ti^{4+} and Mn^{2+} ions in the Mg_2SnO_4 :2 mol% Ti^{4+} and Mg_2SnO_4 :0.1 mol% Mn^{2+} samples, respectively.

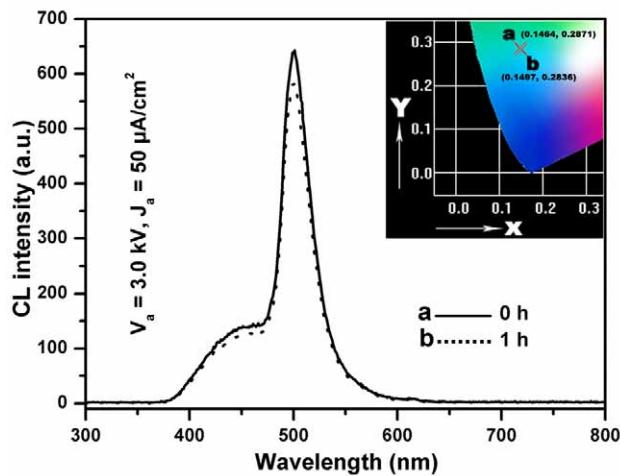


Figure S3. The CL spectra of Mg_2SnO_4 : 0.5 mol% Ti^{4+} , 0.025 mol% Mn^{2+} sample ($V_a = 3.0 \text{ kV}$, $J_a = 50 \mu\text{A}/\text{cm}^2$), and I_a denotes the initial intensity for 0 h, and I_b denotes the intensity after continuous electron beam excitation for 1 h and the inset are their corresponding CIE chromaticity coordinates. $I_b/I_a = 0.92$.

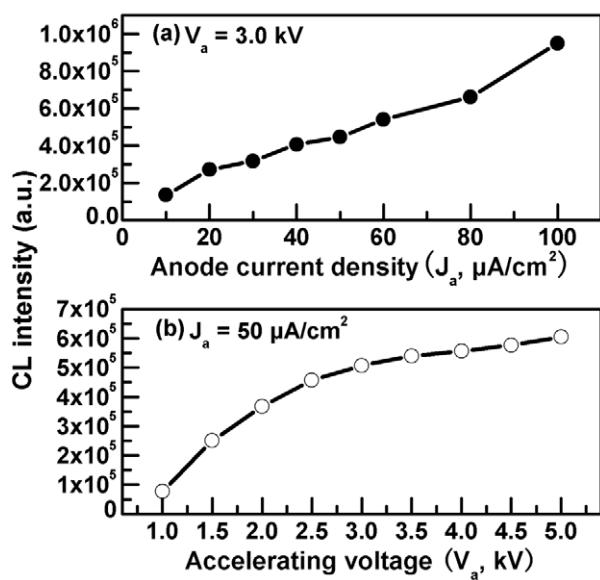


Fig. S4 The CL intensity of the representative Mg_2SnO_4 : 5 mol% Ti^{4+} , 0.025 mol% Mn^{2+} sample as a function of (a) anode current density (J_a) and (b) accelerating voltage (V_a).