Supporting Materials

Reduction of Mn^{4+} to Mn^{2+} in $CaAl_{12}O_{19}$ by co-doping charge compensators to obtain tunable photoluminescence

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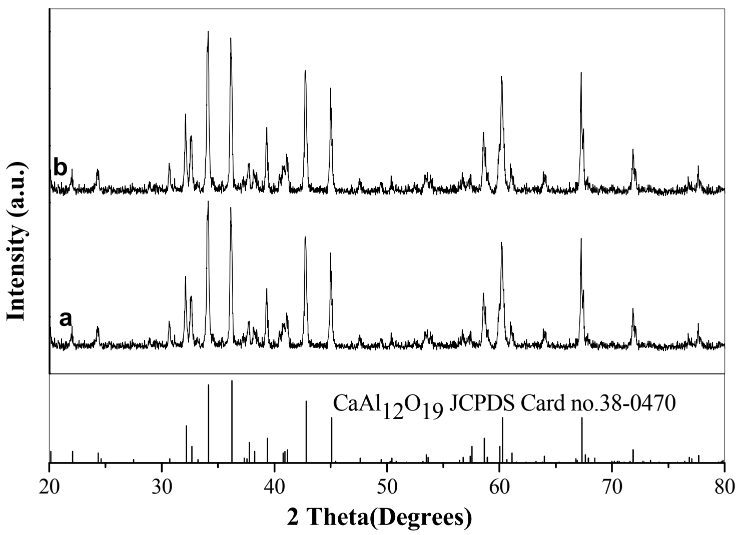

Figure S1. XRD patterns of (a) $CaAl_{12}O_{19}$:0.5%Mn and (b) $CaAl_{12}O_{19}$:0.5%Mn,3%Bi^{3+} sintered at 1500 °C for 3 h in air. XRD data were collected with an X-ray diffractometer (D8 Advance, Bruker, Germany) with graphite monochromatized Cu Kα radiation (λ =0.15406 nm). Identification of phases was made using standard JCPDS files.

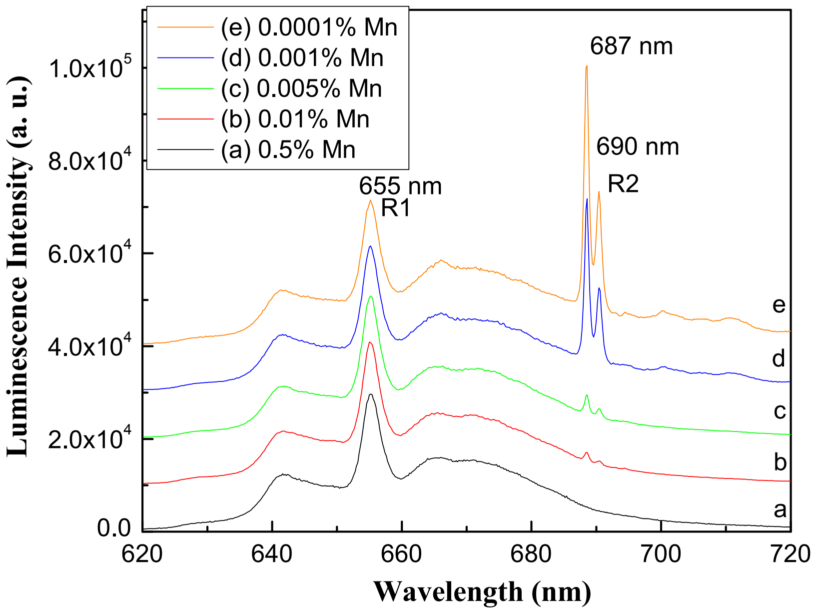

Figure S2. Emission spectra of $CaAl_{12}O_{19}$:Mn^{4+} with different doping concentration at (a) 0.5, (b) 0.01, (c) 0.005, (d) 0.001, (e) 0.0001 mol% of Al^{3+}. The emission spectra were measured on a computer-controlled Triax 320 fluorescence spectrofluorimeter (Jobin-Yvon Inc., Longjumeau, France) with 150 W xenon lamp as the excitation source.

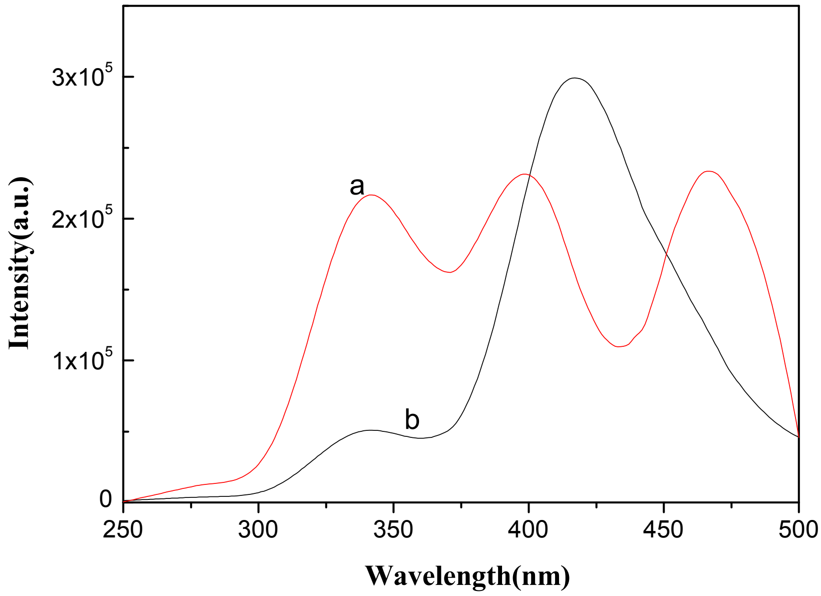

Figure S3. Excitation spectra of CAO:0.001%Mn^{4+} monitored at (a) 655 nm and (b) 687 nm. The excitation spectra were measured on a computer-controlled Triax 320 fluorescence spectrofluorimeter (Jobin-Yvon Inc., Longjumeau, France).

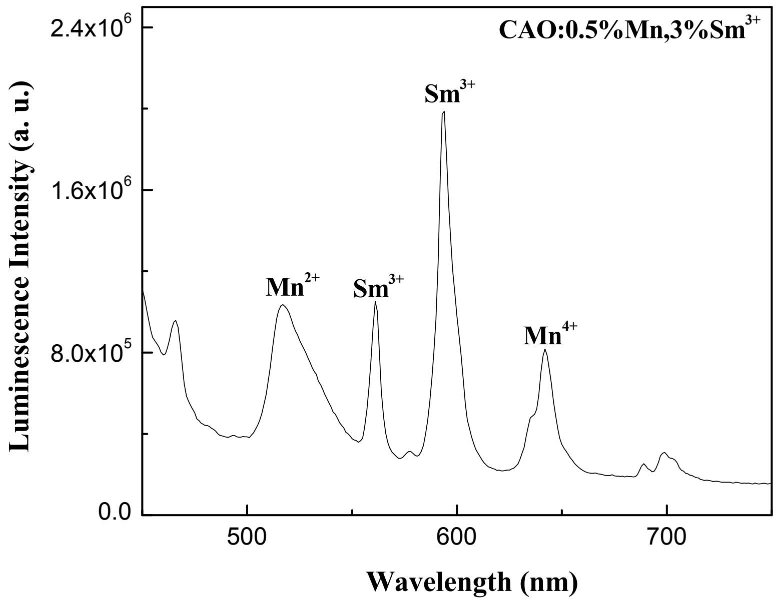

Figure S4. Emission spectrum of $CaAl_{12}O_{19}$:0.5%Mn,3%Sm^{3+} sintered at 1500 °C for 3 h in air. Measurement was performed on fluorescence spectrophotometer (Fluoro Max-4 Horiba Jobin Yvon Holland) at room temperature.

The emission spectrum of $CaAl_{12}O_{19}$:0.5%Mn,3%Sm^{3+} is composed of emission bands from Sm^{3+} at 561 nm and 594 nm, Mn^{2+} at 517 nm , and Mn^{4+} at 655 nm.

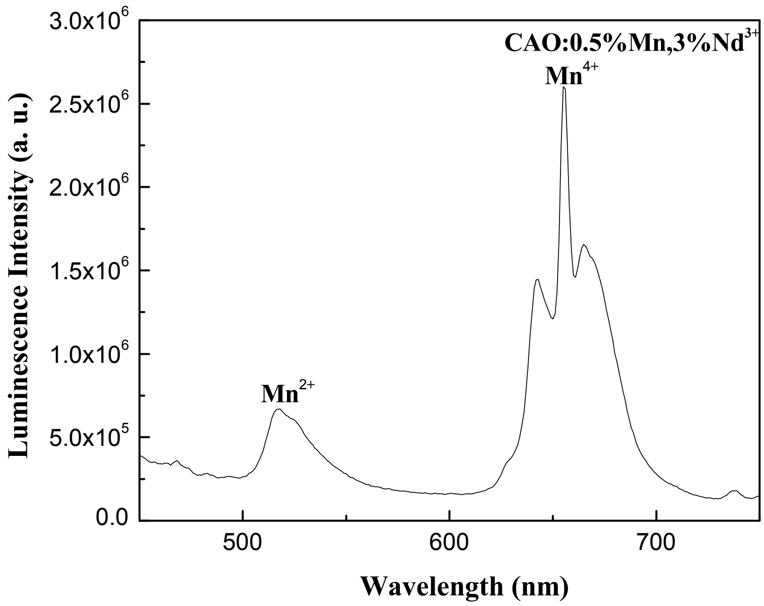

Figure S5. Emission spectrum of $CaAl_{12}O_{19}$:0.5%Mn,3%Nd^{3+} sintered at 1500 °C for 3 h in air. Measurement was performed on fluorescence spectrophotometer (Fluoro Max-4 Horiba Jobin Yvon Holland) at room temperature.

The emission spectrum of $CaAl_{12}O_{19}$:0.5%Mn,3%Nd^{3+} is composed of green (from Mn^{2+}) at 517 nm and red (from Mn^{4+}) emissions at 655 nm.

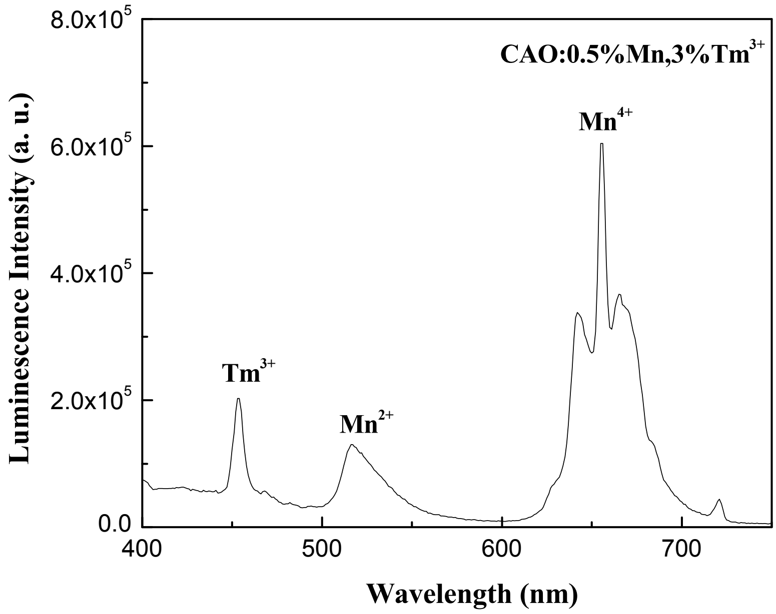

Figure S6. Emission spectrum of $CaAl_{12}O_{19}$:0.5%Mn,3%Tm^{3+} sintered at 1500 °C for 3 h in air. Measurement was performed on fluorescence spectrophotometer (Fluoro Max-4 Horiba Jobin Yvon Holland) at room temperature.

The emission spectrum of $CaAl_{12}O_{19}$:0.5%Mn,3%Tm^{3+} is composed of blue emission (from Tm^{3+}) at 454 nm, green emission (from Mn^{2+}) at 517 nm , and red emission (from Mn^{4+}) at 655 nm.

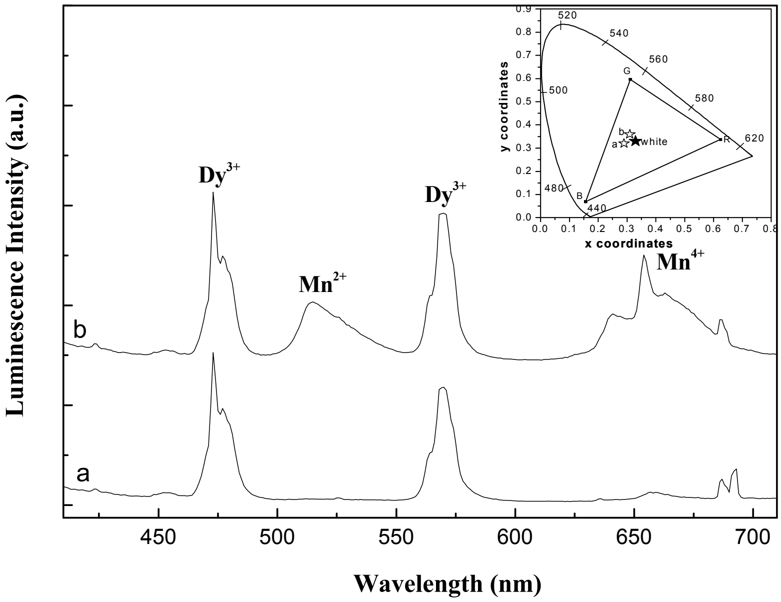

Figure S7. Emission spectra (λex= 395 nm) of the phosphor (a) $CaAl_{12}O_{19}$:3%Dy^{3+} and (b) $CaAl_{12}O_{19}$:0.5%Mn^{4+},3%Dy^{3+}. Inset: CIE chromaticity diagrams of emission spectra of (a) $CaAl_{12}O_{19}$:3%Dy^{3+} and (b) $CaAl_{12}O_{19}$:0.5%Mn^{4+},3% Dy^{3+}.

The emission spectra of CAO:3% Dy^{3+} shows two characteristic emission bands of Dy^{3+}, a blue band of magnetic dipole transition ($^4F_{9/2}$ - $^6H_{15/2}$) and a yellow band of electric dipole transition ($^4F_{9/2}$ - $^6H_{11/2}$) as shown in Fig. 7a. In this phosphor, the electric dipole and magnetic dipole transitions have almost equal intensities because that Dy^{3+} at the Ca^{2+} site has a high-symmetry in the 12-fold coordinated cuboctahedron lattice structure. Both green emission of Mn^{2+} and red emission of Mn^{4+} are observed in the PL spectrum of CAO:Mn co-doped with 3% Dy^{3+}.The CIE chromaticity coordinates of CAO:3%Dy^{3+} and CAO:0.5%Mn, 3%Dy^{3+} are depicted by the inset in Fig. 7. While the CIE of both phosphors fill into the white region, but the co-doped phosphor has a stronger red component, therefore, is more attractive for creating warm white light.