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 K$\alpha$ radiation ($\lambda$=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$_2$,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$_2$,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 ($\lambda_{ex}= 395$ 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.