Supporting information

Design the luminescence pattern via altering crystal structure and doping ions to create warm white LEDs

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Experimental Section

The $Mg_{1.98-y-z}Al_4Si_5O_{18}$(MASO):$0.02Eu^{2+}$,$yMn^{2+}$,$zTb^{3+}$ and $K_{0.24}Mg_2Al_{4.26}Si_{4.74}O_{18}$(KMASO) phosphors were synthesized by a high-temperature solid-state reaction. The constituent oxides or carbonates K_2CO_3(99.9%), MgO (99.9%), Al_2O_3 (99.9%), SiO_2 (99.9%), Eu_2O_3 (99.99%), Tb_4O_7 (99.99%), and $MnCO_3$ (99.99%) were used as the starting materials and weighed according to the stoichiometric ratio, which were mixed homogeneously by an agate mortar for 30 minutes, placed in a crucible with a lid, and then sintered in a tubular furnace at 1350°C for 4 h in reductive atmosphere (10% H_2 + 90% N_2 mixed flowing gas).

Characterization

The structure of the sintered samples was identified by powder X-ray diffraction (XRD) analysis (Bruker AXS D8), with graphite monochromatized Cu Kα radiation ($\lambda = 0.15405$ nm) operating at 40 kV and 40 mA. The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed by using a Hitachi F4500 spectrometer equipped with a 150 W xenon lamp under a working voltage of 700 V. The excitation and emission slits were both set at 2.5 nm. Energy dispersive spectroscopy (EDS) was performed using a field emission scanning electron microscope equipped with an EDS (FE-SEM, S-4800, Hitachi, Japan). The luminescence decay curve was obtained from a Lecroy Wave Runner 6100 digital oscilloscope (1GHz) using a tunable laser (pulse width = 4 ns, gate = 50 ns) as the excitation source (Continuum Sunlite OPO).

Results and Discussion

1. Phase formation

Figure S1 shows the XRD patterns of the typical obtained powders. All the diffraction peaks of obtained samples can be indexed to the corresponding standard data, indicating that obtained samples are single phase and doped ions do not significantly influence the crystal structure. In order to confirm the formula of KMASO, the chemical composition of KMASO:Ce^{3+} phosphors was analyzed. A representative energy dispersive spectroscopy EDS spectrum is also shown in Figure S1. The element ratio K/Mg/Al/Si =0.7:6.24:15.58:15.93 was calculated from the EDS data and is very near to the standard ratio (0.24:2:4.26:4.74), further indicating that the powder are KMASO.

2. Evidence of the energy transfer of the Ce^{3+} - Tb^{3+}, Ce^{3+} - Mn^{2+}, Eu^{2+} - Tb^{3+}, Eu^{2+} - Mn^{2+} luminescent centers.

One of the important measurements for the energy transfer is to test the PLE spectra with monitoring the emission of the acceptor ions and the donor ions. Figure S2 gives the basis of the optical properties of single doped and co-doped ions in the MASO host. As is shown, the PLE spectrum monitoring the emission of the acceptor ions is similar to that monitoring the emission of the donor ions, which is a strong evidence for the energy transfer between these luminescent centers.

Figure S1

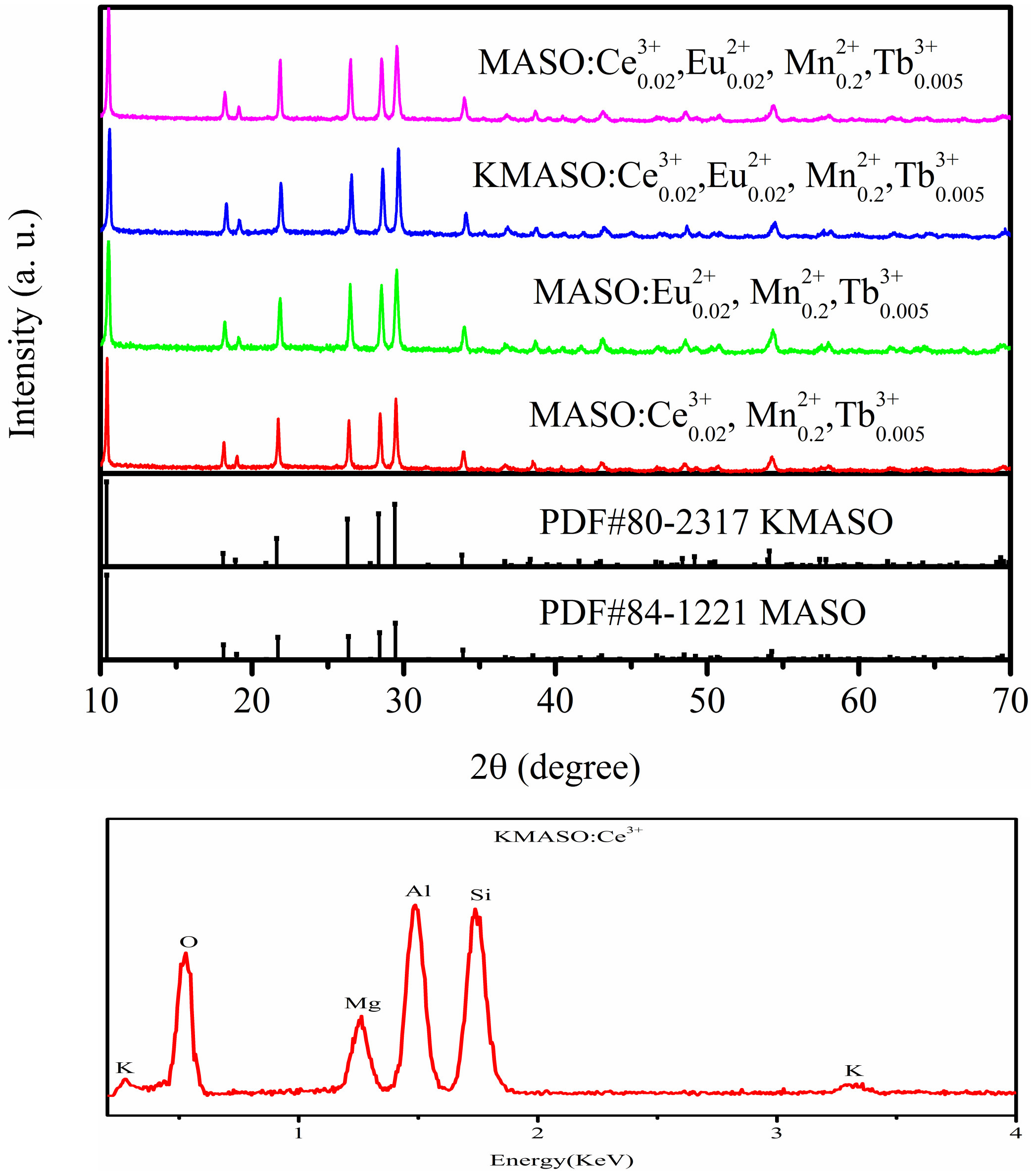

Figure S1. The XRD patterns of the typical obtained powders and the EDS spectrum of KMASO:Ce^{3+}.

Figure S2

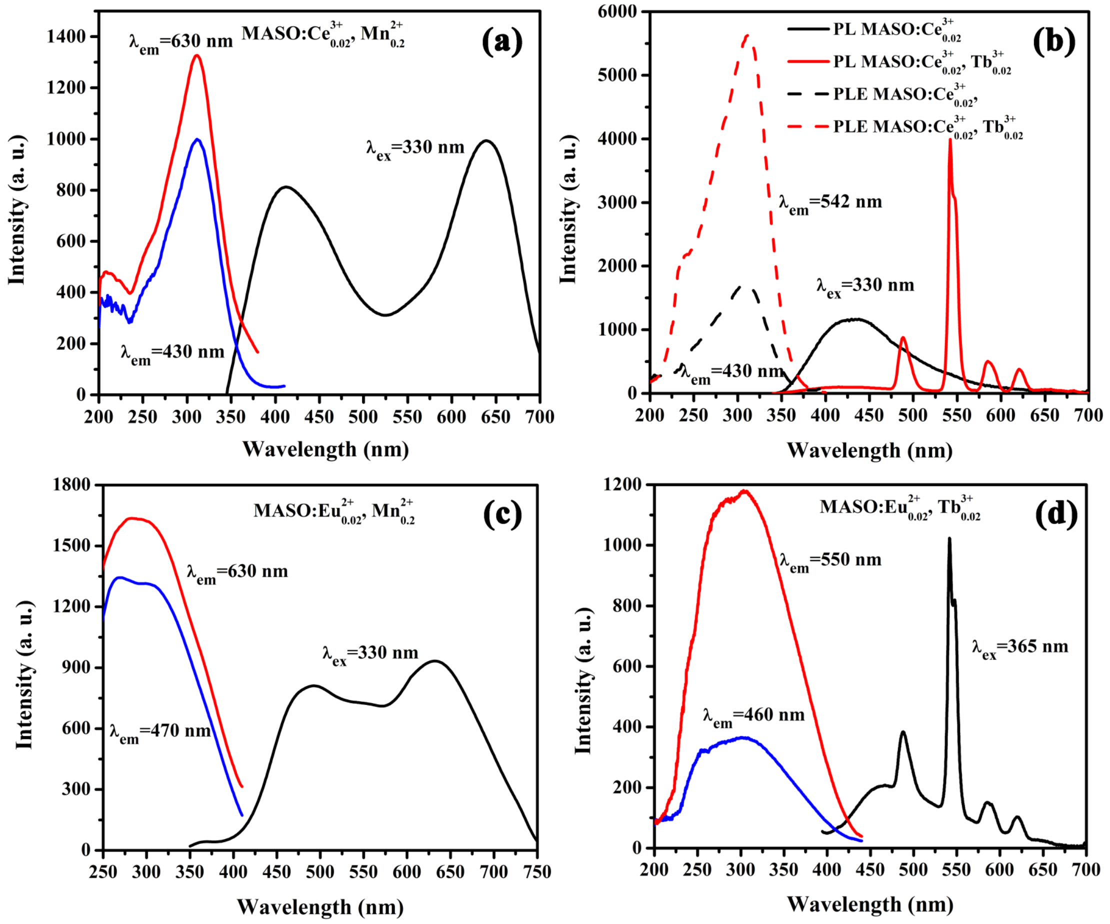

Figure S2. The PL and PLE spectra of MASO:0.02Ce^{3+},0.2Mn^{2+} (a), MASO:0.02Ce^{3+} and MASO:0.02Ce^{3+},0.02Tb^{3+} (b), MASO:0.02Eu^{2+},0.2Mn^{2+} (c), MASO:0.02Eu^{2+},0.02Tb^{3+} (d) phosphors.