

Supporting Information

Green/green-yellow-emitting KSrGd(PO₄)₂:Ce³⁺, Tb³⁺/Mn²⁺ phosphors with high quantum efficiency for LEDs and FEDs

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Experimental details

Gd₂O₃, Ce(NO₃)₃ and Tb₄O₇ (99.999%) were purchased from Science and Technology Parent Company of Changchun Institute of Applied Chemistry and other chemicals were purchased from Beijing Chemical Company. All chemicals were of analytical grade reagents and used directly without further purification.

A series of polycrystalline K₂SrGd(PO₄)₂ (KSG) and different concentrations of Ce³⁺, Tb³⁺, and Mn²⁺-doped KSG samples powder samples were prepared by Pechini-type sol-gel method. The doping concentrations of Ce³⁺, Tb³⁺ and Mn²⁺ were chosen as 0.01 – 0.1, 0.0005 – 0.25 of Gd³⁺ and 0.01 – 0.3 of Sr²⁺ in the KSG host, respectively. Typically, stoichiometric amounts of Gd₂O₃, Ce(NO₃)₃, Tb₄O₇ and Mn(CH₃COO)₂ were dissolved in dilute nitric acid (HNO₃) or deionized water (H₂O) under stirring and heating, resulting in the formation of a colorless solution of Gd(NO₃)₃, Ce(NO₃)₃, Tb(NO₃)₃ and Mn(NO₃)₂, respectively. Firstly, stoichiometric amounts of Sr(NO₃)₂ and the solution of Gd(NO₃)₃ and Ce(NO₃)₃/Tb(NO₃)₃/Mn(NO₃)₂ were mixed together, stirring for 15 min, followed by the citric acid was dissolved in the above solution (citric acid/metal ion = 2:1 in moles). Then, the pH of the solution was adjusted to a low value with HNO₃ followed by the addition of the stoichiometric amounts of KH₂(PO₄)₂ and (NH₄)H₂(PO₄)₂. Finally, a certain amount of polyethylene glycol (PEG, molecular weight = 20000, A.R.) was added as a cross-linking agent ($C_{\text{PEG}} = 0.01 \text{ mol/L}$). The citric acid is used to form stable metal complexes, and its polyesterification with PEG forms a polymeric resin. Immobilization of metal complexes in such rigid organic polymer networks reduces segregation of particular metal ions, ensuring compositional homogeneity. The resultant mixtures were stirred for 1 h and then heated at 75 °C in a water bath until homogeneous gels formed. After

being dried in an oven at 100 °C for 10 h, the gels were ground and pre-fired at 500 °C for 4 h in air. Then the samples were fully ground and calcined at the desired temperature (1000 °C) in air for 4 h. The obtained powders were then reduced at 800 °C for 2 h under a 5% H₂/95% N₂ atmosphere to produce the final samples.

Characterization

The X-ray diffraction (XRD) measurements were carried out on a D8 Focus diffractometer using Cu K α radiation ($\lambda = 0.15405$ nm). High-resolution transmission electron microscopy (HRTEM) was performed using PEI Tecnai G2 S-Twin with a field emission gun operating at 200 kV. Images were acquired digitally on a Gatan multipole CCD camera. Energy-dispersive X-ray (EDX) spectra were obtained using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi) equipped with an energy-dispersive X-ray spectrum (EDS, JEOL JXA-840). The PL measurements were performed on a Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The CL measurements were carried out in an ultra-high vacuum chamber ($< 10^{-8}$ Torr), where the phosphors were excited by an electron beam in the voltage range of 3.0 – 5.5 kV and different filament currents (75 – 90 mA), and the emission spectra were recorded using an F-7000 spectrophotometer. Absolute photoluminescence quantum yields (QYs) were measured by absolute PL quantum yield measurement system (C9920-02, Hamamatsu Photonics K. K., Japan). The luminescence decay curves were obtained from a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) using a tunable laser (pulse width = 4 ns, gate = 50 ns) as the excitation (Continuum Sunlite OPO). All the measurements were performed at room temperature (RT).

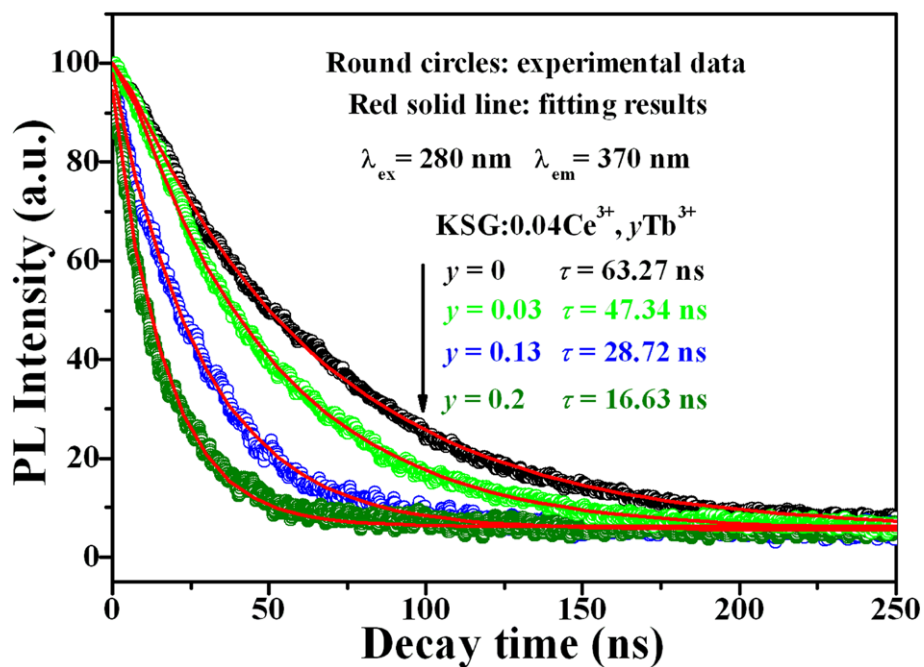


Fig. S1. The decay curves and lifetimes of Ce³⁺ ions in KSG:0.04Ce³⁺, yTb³⁺ samples with changing Tb³⁺ (y = 0, 0.03, 0.13 and 0.2) concentrations.

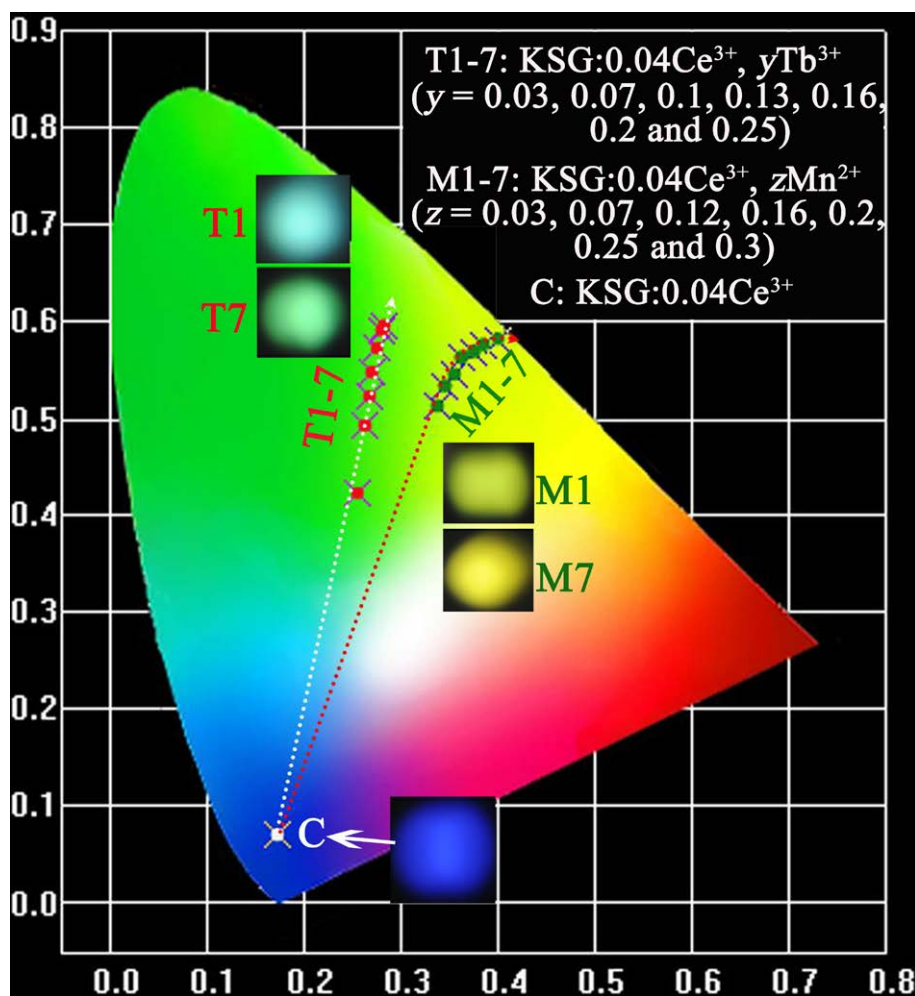


Fig. S2. The variation of the CIE chromaticity coordinates of KSG:0.04Ce³⁺, KSG:0.04Ce³⁺, yTb³⁺ and KSG:0.04Ce³⁺, zMn²⁺ samples with changing Tb³⁺ (y = 0.03 – 0.25) and Mn²⁺ (z = 0.03 – 0.3) concentrations and the representative digital luminescence photographs under low voltage electron beam excitation.

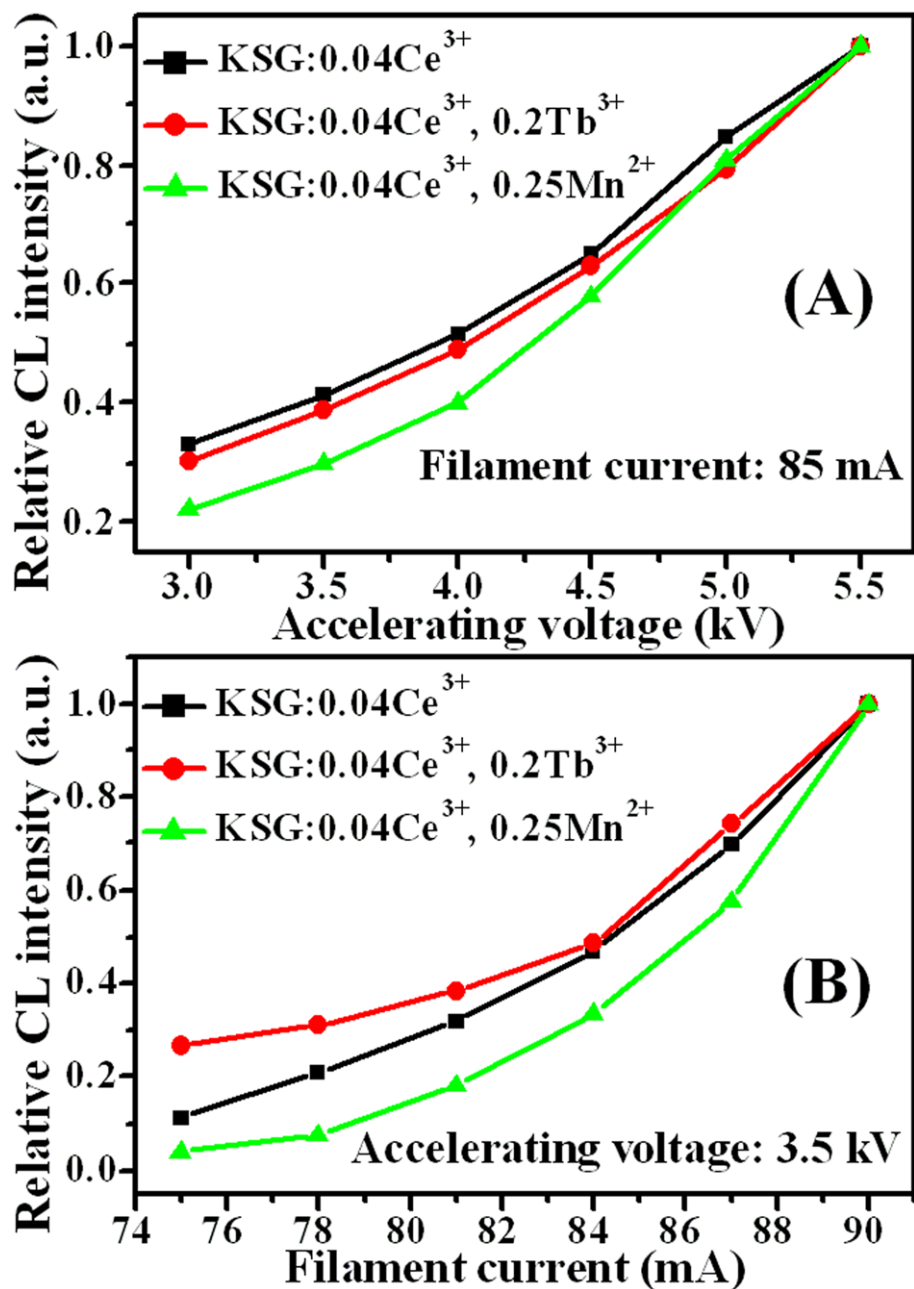


Fig. S3. Cathodoluminescence intensities of Ce³⁺, Tb³⁺ and Mn²⁺-activated KSG samples as a function of accelerating voltage (A) and filament current (B).