

Supporting Information

Green Lighting Upconversion in Yb³⁺, Er³⁺ Co-doped PbWO₄Jun Ho Chung, Sang Yeup Lee, Jong Won Eun, Kwang Bo Shim, and Jeong Ho Ryu^{†,*}

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Experimental Procedure

PbWO₄:Er³⁺/Yb³⁺ powder samples were prepared by the traditional solid-state reaction method. The starting materials were PbO (Kojundo Chemical, 99.99%), WO₃ (Kojundo Chemical, 99.99%), Er₂O₃ (Shinetsu Chemical 99.99%) and Yb₂O₃ (Shinetsu Chemical 99.99%). The molar ratios of the cations were as follows: (1-x-y)Pb²⁺ + xEr³⁺ + yYb³⁺ + W⁶⁺, x = 0.001, 0.01, 0.02, 0.03 and 0.05, y = 0.08. In this work, the Yb³⁺ concentration was fixed to be 8 mol % for detailed investigation on effects of Er³⁺ concentration ranged from 0.1 to 5 mol %. After mixing, the obtained mixtures were calcined at 1000 °C for 5 hrs in ambient atmosphere. The crystalline phases of the calcined powders samples were identified by X-ray powder diffraction (XRD), operating at 40 kV using Cu-Kα radiation (λ = 1.5406 Å). The UC luminescent spectra and power dependent properties were evaluated using a Photoluminescence spectroscopy (Perkin-Elmer, LS55, USA) in room temperature with range of wavelength from 400 nm to 700 nm under excitation (980 nm) and pump power for irradiation varied from 20 to 110 mW (SPEX, France).

XRD Result

Supporting Figure 1(a) shows phase identification of the PbWO₄:Er³⁺/Yb³⁺ samples with various Er³⁺ concentrations calcined at 1000 °C for 5 hrs. The prominent peaks indicated corresponded well to scheelite-type PbWO₄ phase (JCPDS 19-0708) in all Er³⁺ concentrations. No impurities or secondary phases could be identified from the XRD patterns in the limit of XRD resolution, thus suggesting that single crystallized PbWO₄:Er³⁺/Yb³⁺ with various Er³⁺/Yb³⁺ concentrations up to 5/8 mol% can be obtained *via* the solid-state reaction. The Pb²⁺ and W⁶⁺ atoms coordinate with eight and four O atoms, respectively.

Based on the effective ionic radii of cations with different coordination numbers (CN) and large charge difference between Pb²⁺ ion and W⁶⁺ ion, it can be expected that Er³⁺ and Yb³⁺ [*r*(Er³⁺) = 1.004 Å, *r*(Yb³⁺) = 0.985 Å, when CN = 8] are preferably substituted into the Pb²⁺ sites [*r*(Pb²⁺) = 1.29 Å, when CN = 8] compared to the W⁶⁺ site [*r*(W⁶⁺) = 0.66 Å, when CN = 4]. It is worth noting that when the Pb²⁺

ions is substituted by the Er³⁺ or Yb³⁺ ions with smaller ionic radius than Pb²⁺, the corresponding lattice constant becomes smaller. Supporting Figure 1(b) shows the diffraction peak broadening of (112) plane near 2θ = 27.6°, which clearly indicates structural variation as a function of Er³⁺ concentration. In particular, it is seen that the diffraction peaks shift to higher 2θ angle indicating the shrink of lattice constants by substitution of smaller Er³⁺ ions into Pb²⁺ ion sites.

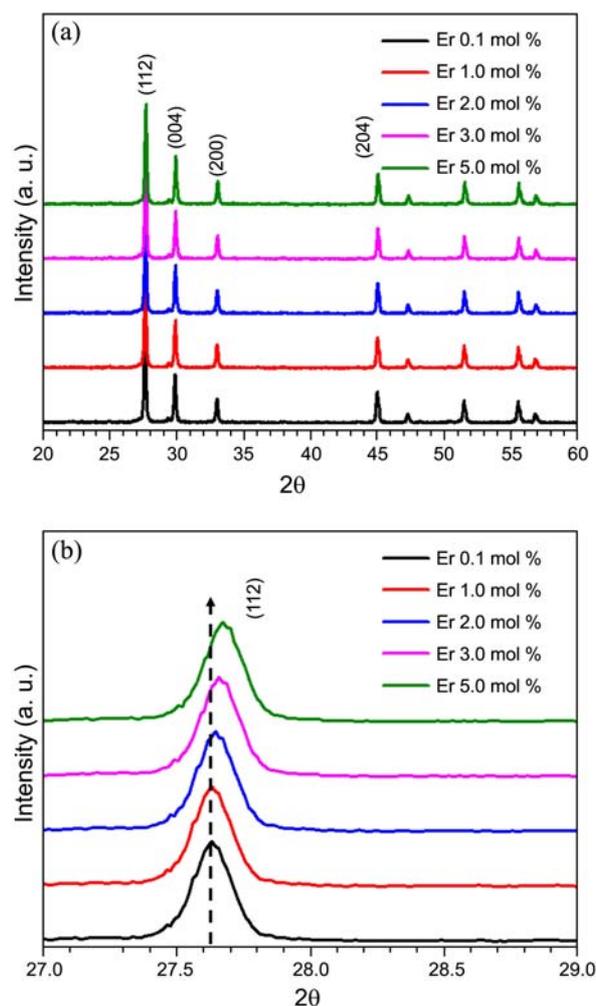


Figure 1. (a) X-ray diffraction patterns of Er³⁺/Yb³⁺ co-doped PbWO₄ upconversion phosphors with various Er³⁺ concentrations. (b) The enlarged XRD patterns near 2θ = 27.6° for (112) peak.