

Electronic Supplementary Information for:

Negligible concentration quenching in photoluminescent nanocrystals with high photoactive rare-earth concentrations: silica-(Tb,Ce)PO₄ transparent glass-ceramic green phosphors

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Experimental procedure

A dilute aqueous solution of nitric acid was added to 25 mmol (5.2 g) of tetraethoxysilane (TEOS, Shin-Etus Chemical) at a TEOS : H₂O : HNO₃ molar ratio of 1 : 1.83–1.87 (= x_1) : 0.002 and stirred for 55 min at 20 °C in a sealed plastic container to form a clear solution. Triphenylphosphine oxide (TPPO, Tokyo Chemical Industry) was added and stirred another 5 min to form a clear solution. This solution was further mixed with an aqueous solution of ammonium acetate (AcONH₄, Wako Pure Chemical), terbium acetate ((AcO)₃Tb, 99.9%, Wako Pure Chemical), cerium acetate ((AcO)₃Ce, 99.99 %, Rare Metallic), and neodymium acetate ((AcO)₃Nd, 99.9 %, Wako Pure Chemical). The overall TEOS : H₂O : HNO₃ : AcONH₄ : (AcO)₃Tb + (AcO)₃Ce + (AcO)₃Nd : TPPO molar ratio was 1 : 10 (= $x_1 + x_2$) : 0.002 : 0.01 : 0.01 (= $z_{RE} = z_{Tb} + z_{Ce} + z_{Nd}$) : z_P . The molar ratio of RE acetates was fixed at $z_{Tb} : z_{Ce} = 98 : 2$ (2 at % Ce) for the Nd-free samples and $z_{Tb} : z_{Ce} : z_{Nd} = 97 : 2 : 1$ (2 at % Ce and 1 at % Nd) for the Nd-doped sample. After stirring for 2 min, the stir bar was removed and the resultant clear solution was maintained at 20 °C until gelation. The gel was aged for 1 day at 60 °C. The container was then opened, solvent phase was discarded, and the wet gel was gently dried at 60 °C. The dried gels were sintered in a tube furnace heated at a rate of 200 °C h⁻¹ and held at 1200 °C up to 1 h. The sintering atmosphere was changed from air to He at 600 °C. Hydrogen reduction was conducted by additionally introducing a small amount (5 %) of H₂ between 800 and 1200 °C. Two parallel faces of sintered glasses were polished to an optical finish.

Optical absorption and Raman spectra were acquired using a conventional spectrometer (U-4100, Hitachi) and Raman spectrometer (NRS-4500, JASCO, excitation at 532 nm), respectively. Photoluminescence (PL) spectra were recorded using an integrating sphere (4P-GPS-033-SL, Labsphere) connected to a fluorophotometer (F-7000, Hitachi) used as a light source and a CCD spectrometer (BLACK-Comet, StellarNet). PL intensity was calibrated using a photodiode power meter (PD300R-UV, OPHIR). The areas of the emission and excitation bands in the PL spectra obtained by directly illuminating the sample define the number of emitted photons, N_{em} , and the number of photons not absorbed by the sample, N_{ex} , respectively. The area of the excitation band for an empty sphere corresponds to the number of photons from the light source, N_{ex}^0 . Absorption factor (f_A), internal quantum efficiency (IQE), and external quantum efficiency (EQE) were defined as $f_A = (N_{ex}^0 - N_{ex})/N_{ex}^0$, $IQE = N_{em}/(N_{ex}^0 - N_{ex})$, and $EQE = f_A \times IQE = N_{em}/N_{ex}^0$, respectively. The experimental uncertainties of f_A , IQE, and EQE were ± 2 %. The PL decay curves of the $^5D_4 \rightarrow ^7F_j$ ($j = 4, 5$) transitions of Tb³⁺ ions were recorded using a photomultiplier (R955, Hamamatsu Photonics) covered by a 532 nm long-pass edge filter (LP03-532RU-25, Semrock) and color filter (G545, HOYA), and connected to an oscilloscope. Excitation light from an ultraviolet light-emitting diode (~ 0.35 mW at ~ 290 nm)

was periodically cut with an optical chopper. In these PL measurements a commercial (La,Tb,Ce)PO₄ green phosphor powder (NP-220-02, Nichia) was used as a reference. Several samples were crushed and subject to observations by a transmission electron microscope (TEM, JEM-3200FS, JEOL, operated at 300 kV).

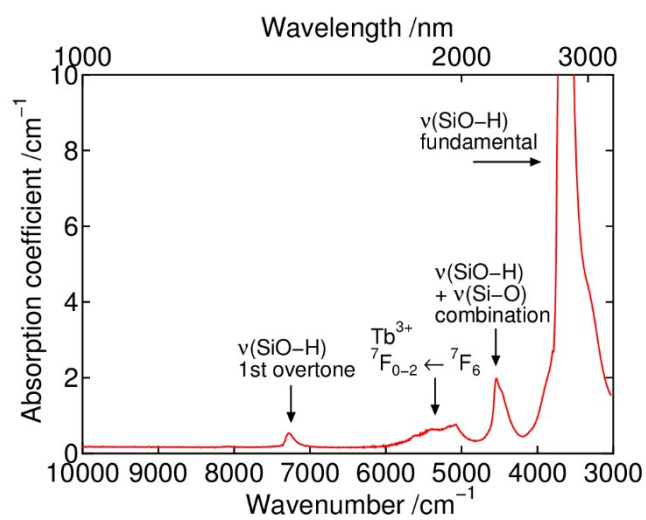


Fig. S1 Near-infrared optical absorption spectrum of glass-ceramic prepared $z_P/z_{RE} = 2.0$ and sintered in He-H₂

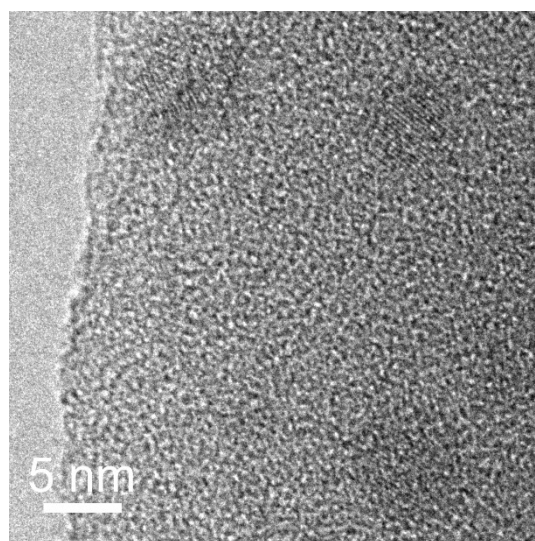


Fig. S2 TEM image of glass-ceramic prepared at $z_P/z_{RE} = 2.0$ and sintered in He-H₂.

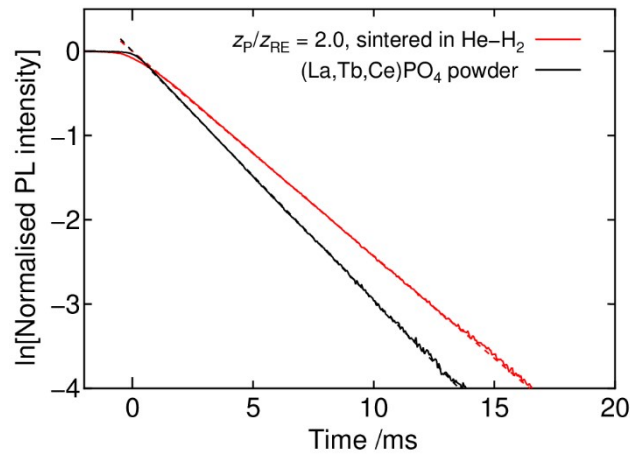


Fig. S3 PL decay curves of the ${}^5D_4 \rightarrow {}^7F_j$ ($j = 4, 5$) transitions of Tb^{3+} ions in glass-ceramic prepared at $z_p/z_{RE} = 2.0$ and sintered in He-H₂, and (La,Tb,Ce)PO₄ phosphor powder under excitation at 290 nm. Dashed lines denote single-exponential functions fitted to observed decay curves.

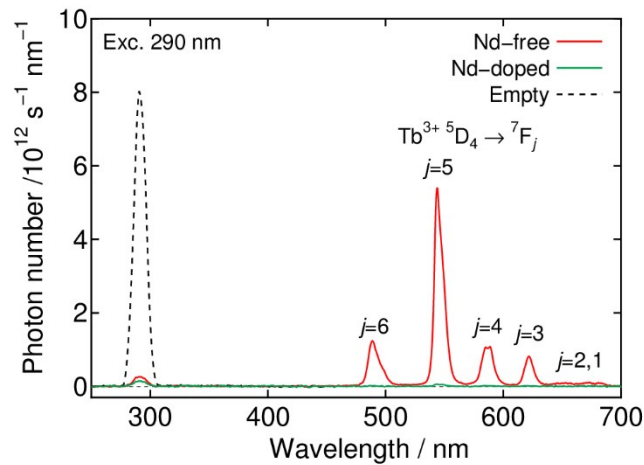


Fig. S4 PL spectra of silica-(Tb,Ce)PO₄ (Nd-free) and silica-(Tb,Ce,Nd)PO₄ (Nd-doped) glass-ceramics prepared at $z_{Ce}/z_{RE} = 0.02$ and $z_p/z_{RE} = 2.0$, and sintered in He-H₂. The Nd-doped sample was prepared at $z_{Nd}/z_{RE} = 0.01$. The spectra of the Nd-free sample and empty sphere are identical to those shown in Fig. 5.