Electronic Supporting Information

Nanocrystallization of Lanthanide-Doped KLu_2F_7-KYb_2F_7 Solid-Solutions in Aluminosilicate Glass for Upconverted Solid-State-Lighting and Photothermal Anti-Counterfeiting

Shaoxiong Wang[a,b,c], Jiangkun Chen[a,b,c], Jidong Lin[a,b,c], Changbin Yang[a,b,c], Feng Huang[a,b,c], Daqin Chen[a,b,c,*]

[a] College of Physics and Energy, Fujian Normal University, Fujian Provincial Key Laboratory of Quantum Manipulation and New Energy Materials, Fuzhou, 350117, China

[*]Corresponding author. E-Mail: dqchen@fjnu.edu.cn

[b] Fujian Provincial Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Xiamen, 361005, China

[c] Fujian Provincial Engineering Technology Research Center of Solar Energy Conversion and Energy Storage, Fuzhou, 350117, China

Table S1 Nominal glass compositions (mol%) for the investigated samples and the corresponding crystallization phases after heat-treatment at 750 ℃ for 2h. Cub and orth represent cubic and orthorhombic phases, respectively.

Glass compositions (mol%)	Crystallization phase	
	As-quenched	Heat-treatment (750°C/2h)
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9LaF_3$	Cub-$K(Lu/La)_3F_{10}$	Cub-$K(Lu/La)_3F_{10}$
$100SiO_2$-$6Al_2O_3$-$9K_2O$ -19KF-$16LuF_3$-$9CeF_3$	Cub-$K(Lu/Ce)_3F_{10}$	Cub-$K(Lu/Ce)_3F_{10}$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9PrF_3$	Cub-$K(Lu/Pr)_3F_{10}$	Cub-$K(Lu/Pr)_3F_{10}$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9NdF_3$	Cub-$K(Lu/Nd)_3F_{10}$	Cub-$K(Lu/Nd)_3F_{10}$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9SmF_3$	Cub-$K(Lu/Sm)_3F_{10}$	Cub-$K(Lu/Sm)_3F_{10}$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9EuF_3$	Cub-$K(Lu/Eu)_3F_{10}$	Cub-$K(Lu/Eu)_3F_{10}$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9GdF_3$	Cub-$K(Lu/Gd)_3F_{10}$	Cub-$K(Lu/Gd)_3F_{10}$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9TbF_3$	Cub-$K(Lu/Tb)_3F_{10}$+ Orth-$K(Lu/Tb)_2F_7$	Cub-$K(Lu/Tb)_3F_{10}$+ Orth-$K(Lu/Tb)_2F_7$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9DyF_3$	Cub-$K(Lu/Dy)_3F_{10}$+ Orth-$K(Lu/Dy)_2F_7$	Cub-$K(Lu/Dy)_3F_{10}$+ Orth-$K(Lu/Dy)_2F_7$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9HoF_3$	Cub-$K(Lu/Ho)_3F_{10}$+ Orth-$K(Lu/Ho)_2F_7$	Cub-$K(Lu/Ho)_3F_{10}$+ Orth-$K(Lu/Ho)_2F_7$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9YF_3$	Cub-$K(Lu/Y)_3F_{10}$+ Orth-$K(Lu/Y)_2F_7$	Cub-$K(Lu/Y)_3F_{10}$+ Orth-$K(Lu/Y)_2F_7$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9ErF_3$	Orth-$K(Lu/Er)_2F_7$	Orth-$K(Lu/Er)_2F_7$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9TmF_3$	Orth-$K(Lu/Tm)_2F_7$	Orth-$K(Lu/Tm)_2F_7$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9YbF_3$	Orth-$K(Lu/Yb)_2F_7$	Orth-$K(Lu/Yb)_2F_7$
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9LuF_3$	Orth-KLu_2F_7	Orth-KLu_2F_7
$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9ScF_3$	Orth-$K(Lu/Sc)_2F_7$	Orth-$K(Lu/Sc)_2F_7$

Table S2 Effective ionic radius of Ln^{3+} in fluorine environment (Z=6)

Lanthanide ions	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}
Radius (Å)	1.19	1.15	1.14	1.12	1.10	1.109	1.08	1.06
Lanthanide ions	Dy^{3+}	Ho^{3+}	Y^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}	Sc^{3+}
Radius (Å)	1.05	1.04	1.04	1.03	1.02	1.01	1.00	0.89

Table S3 Nominal glass compositions (mol%) for the Lu-Yb solid-solution NCs@glass samples and the corresponding crystallization phases after heat-treatment at 750 ℃ for 2h. Orth represents orthorhombic phases.

Samples	Glass compositions (mol%)	Crystallization phase GC (750℃/2h)
0%Yb	$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$24LuF_3$-$0YbF_3$-0.48Er	Orth-KLu_2F_7
10%Yb	$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$21.6LuF_3$-$2.4YbF_3$-0.48Er	Orth-$K(Lu/Yb)_2F_7$
20%Yb	$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$19.2LuF_3$-$4.8YbF_3$-0.48Er	Orth-$K(Lu/Yb)_2F_7$
30%Yb	$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16.8LuF_3$-$7.2YbF_3$-0.48Er	Orth-$K(Lu/Yb)_2F_7$
40%Yb	$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$14.4LuF_3$-$9.6YbF_3$-0.48Er	Orth-$K(Lu/Yb)_2F_7$
50%Yb	$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$12LuF_3$-$12YbF_3$-0.48Er	Orth-$K(Lu/Yb)_2F_7$
60%Yb	$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$9.6LuF_3$-$14.4YbF_3$-0.48Er	Orth-$K(Lu/Yb)_2F_7$
70%Yb	$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$7.2LuF_3$-$16.8YbF_3$-0.48Er	Orth-$K(Lu/Yb)_2F_7$
80%Yb	$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$4.8LuF_3$-$19.2YbF_3$-0.48Er	Orth-$K(Lu/Yb)_2F_7$
90%Yb	$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$2.4LuF_3$-$21.6YbF_3$-0.48Er	Orth-$K(Lu/Yb)_2F_7$
100%Yb	$100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$0LuF_3$-$24YbF_3$-0.48Er	Orth-KYb_2F_7

Table S4 Color coordinates for laser power dependent UC luminescence yielded from the Er: KYb_2F_7 NCs@glass under irradiation of 980 nm laser.

Laser power density (W/cm^2)	CIE x	CIE y
23	0.5407	0.4437
66	0.5318	0.4558
113	0.5166	0.4630
159	0.4943	0.4860
211	0.4650	0.5110
245	0.4336	0.5313
276	0.4284	0.5411

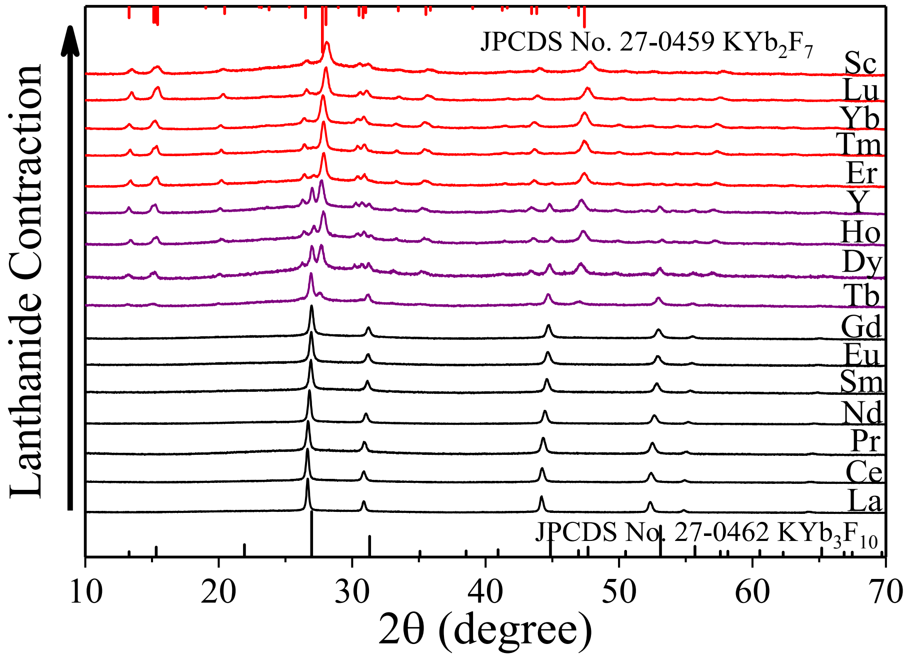

Figure S1 XRD patterns of a series of PGs containing Ln^{3+} dopants (Ln=La-Lu, Sc). The diffraction bars represent cubic KYb_3F_{10} (JPCDS No. 27-0462) and orthorhombic KYb_2F_7 (JPCDS No. 27-0459) crystals. Lu-Ln solid-solution fluorides have precipitated inside glass, indicating that self-crystallization has already occurred in these precursor glasses.

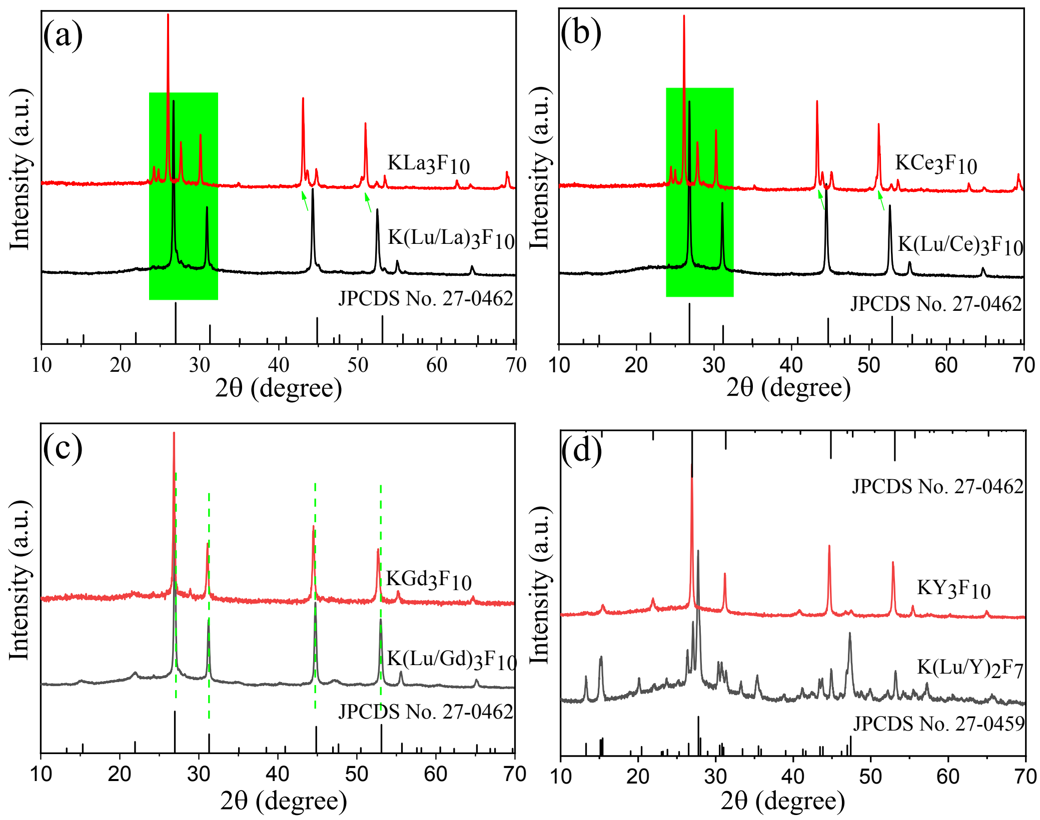

Figure S2 Comparison of XRD patterns of NCs@glass samples with/without the addition of LuF_3. The glass compositions without LuF_3 are $100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$25LnF_3$: (a) Ln=La, (b) Ln=Ce, (c) Ln=Gd, and (d) Ln=Y. The diffraction bars represent cubic KYb_3F_{10} (JPCDS No. 27-0462) and orthorhombic KYb_2F_7 (JPCDS No. 27-0459) crystals. With the addition of LuF_3, the diffraction peaks shift towards large angles, pure cubic phases are obtained for Lu-La, Lu-Ce and Lu-Gd samples and extra orthorhombic phase occurs for Lu-Y sample, verifying that the crystallized phases in glasses are indeed Lu-Ln fluoride solid-solutions and Lu^{3+} ions are beneficial for the growth of pure $K(Lu/Ln)_3F_{10}$ or $K(Lu/Ln)_2F_7$ solid-solutions.

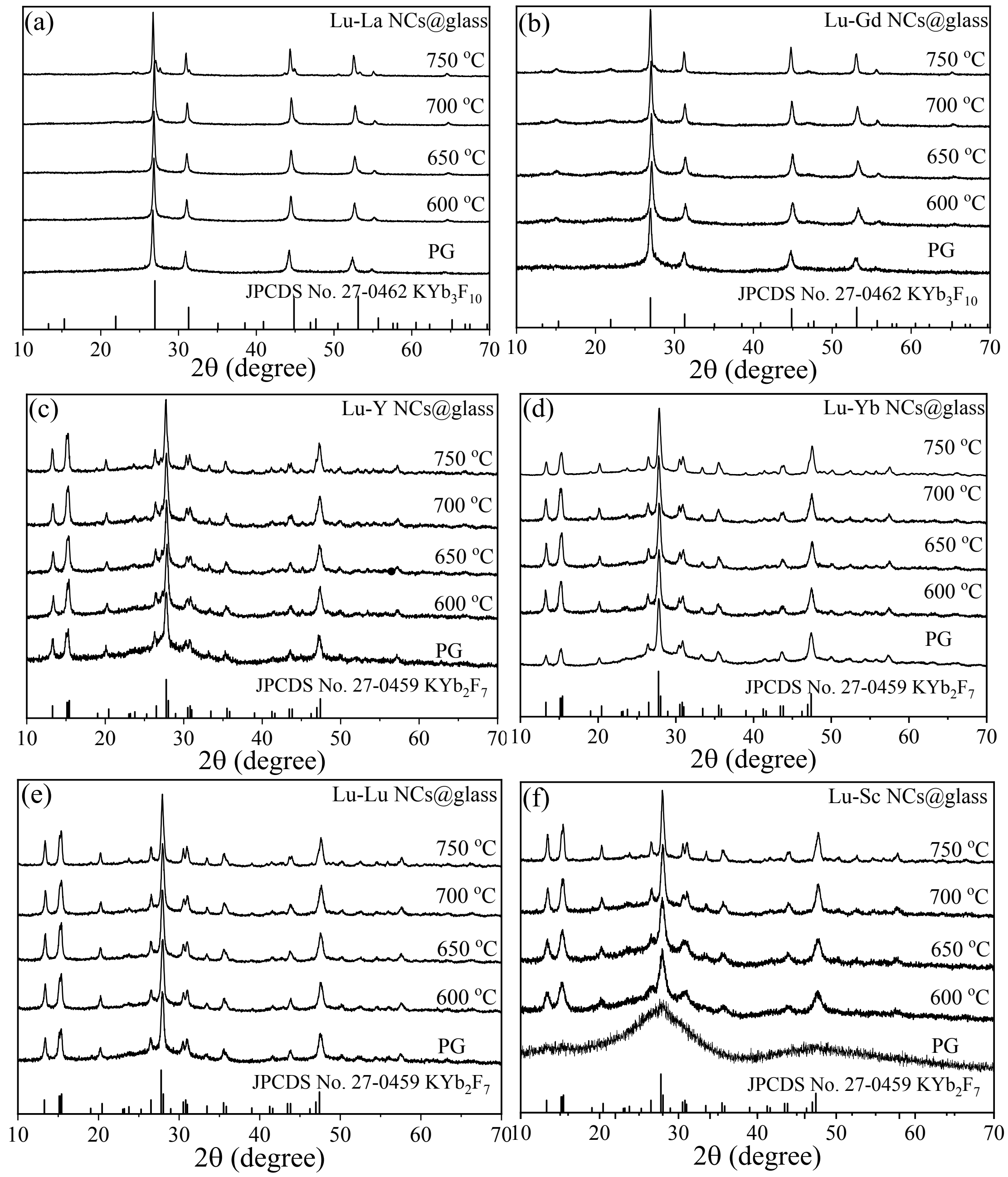

Figure S3 XRD patterns of PGs and Lu-Ln NCs@glass samples prepared by heat-treatment at various temperatures (600, 650, 700, 750 °C) for 2 h: (a) Ln=La, (b) Ln=Gd, (c) Ln=Y, (d) Ln=Yb, (e) Ln=Lu and (f) Ln=Sc.

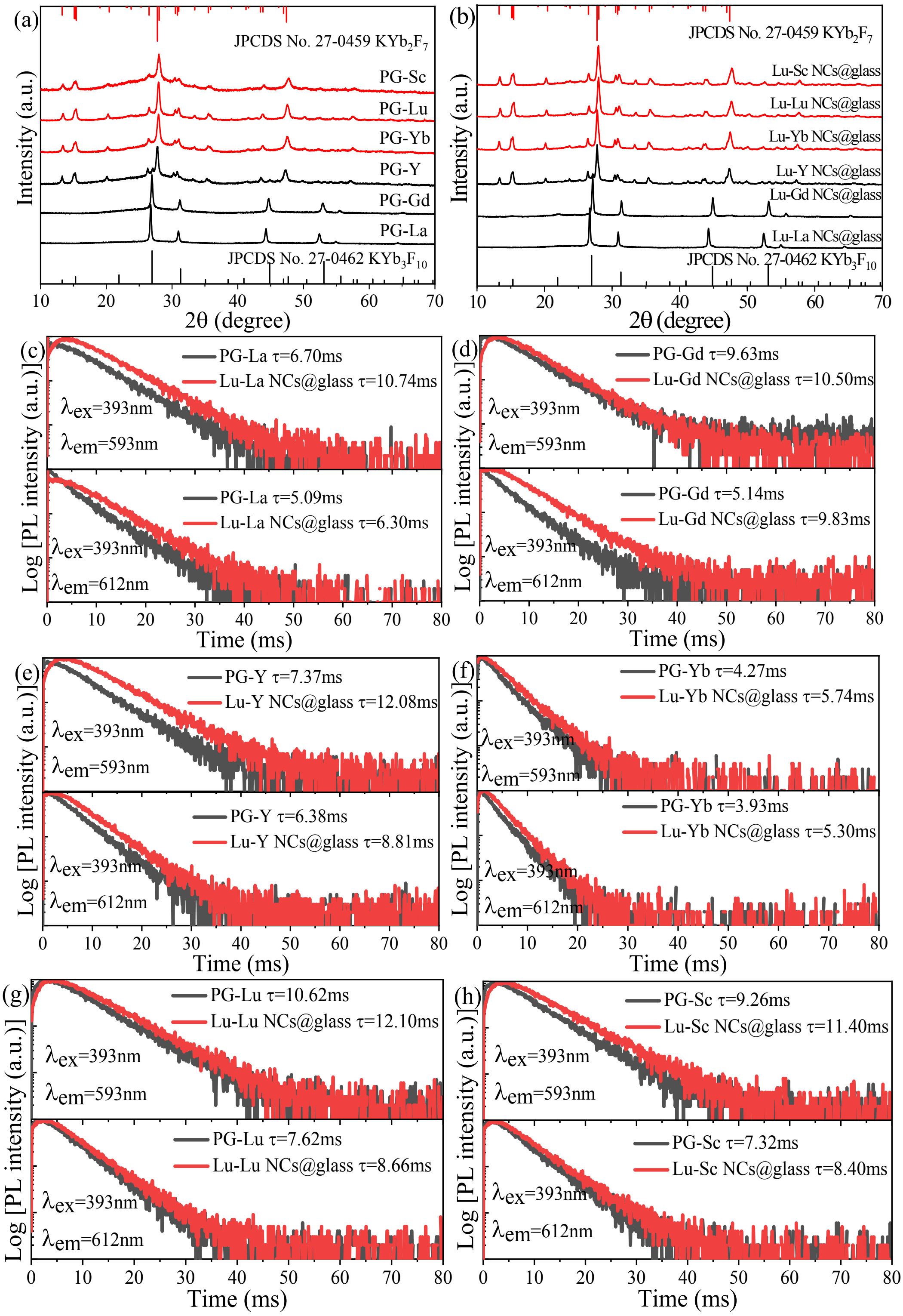

Figure S4 XRD patterns of (a) Eu^{3+} doped PGs and (b) Lu-Ln NCs@glass samples prepared by heating PGs at 750 ℃ for 2 h. Decay curves (λ_{ex}=393 nm) for the corresponding samples by monitoring Eu^{3+} $^5D_0\rightarrow{}^7F_1$ (λ_{em}=593 nm) and $^5D_0\rightarrow{}^7F_2$ (λ_{em}=612 nm) transitions, respectively: (c) Ln=La, (d) Ln=Gd, (e) Ln=Y, (f) Ln=Yb, (g) Ln=Lu and (h) Ln=Sc.

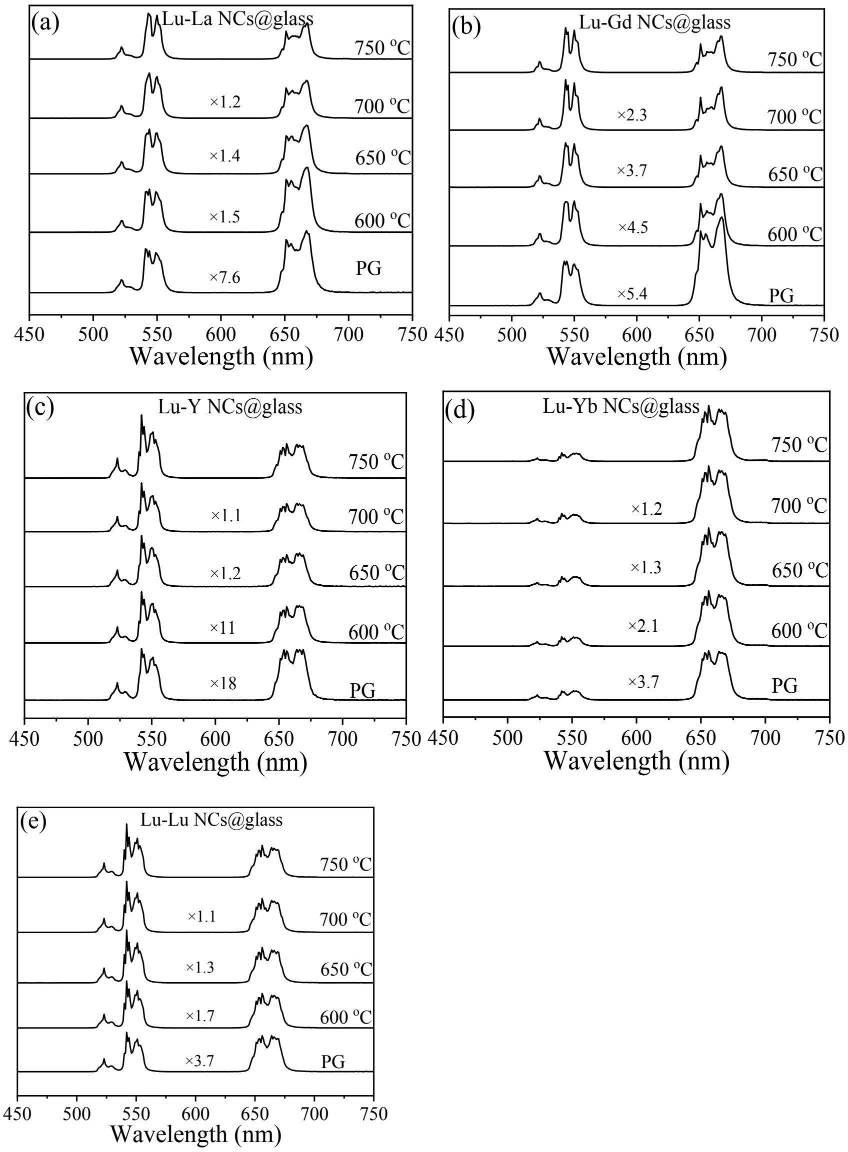

Figure S5 UC emission spectra (λ_{ex} = 980 nm) of PGs and Lu-Ln NCs@glass samples prepared by heat-treatment at various temperatures (600, 650, 700, 750 ºC) for 2 h: (a) Ln=La, (b) Ln=Gd, (c) Ln=Y, (d) Ln=Yb and (e) Ln=Lu. The glass compositions (mol %) are $100SiO_2$-$6Al_2O_3$-$9K_2O$-19KF-$16LuF_3$-$9LnF_3$-$1YbF_3$-$0.32ErF_3$ (Ln=La, Gd, Y, Yb, Lu).

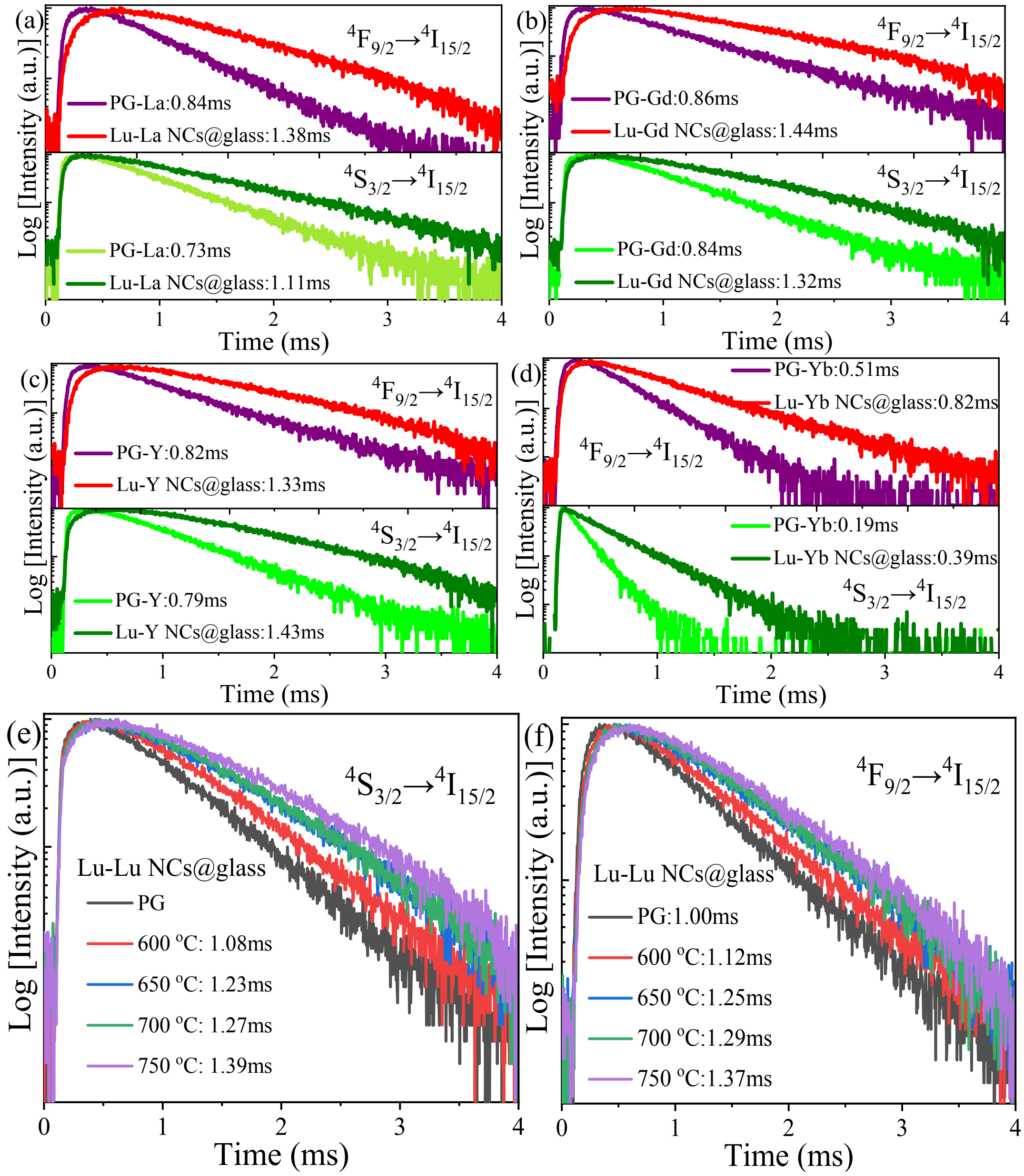

Figure S6 UC decay curves of PGs and Lu-Ln NCs@glass samples by monitoring Er^{3+} green ($^4S_{3/2}\rightarrow^4I_{15/2}$) and red ($^4F_{9/2}\rightarrow^4I_{15/2}$) emissions, respectively: (a) Ln=La, (b) Ln=Gd, (c) Ln=Y, (d) Ln=Yb and (e, f) Ln=Lu.

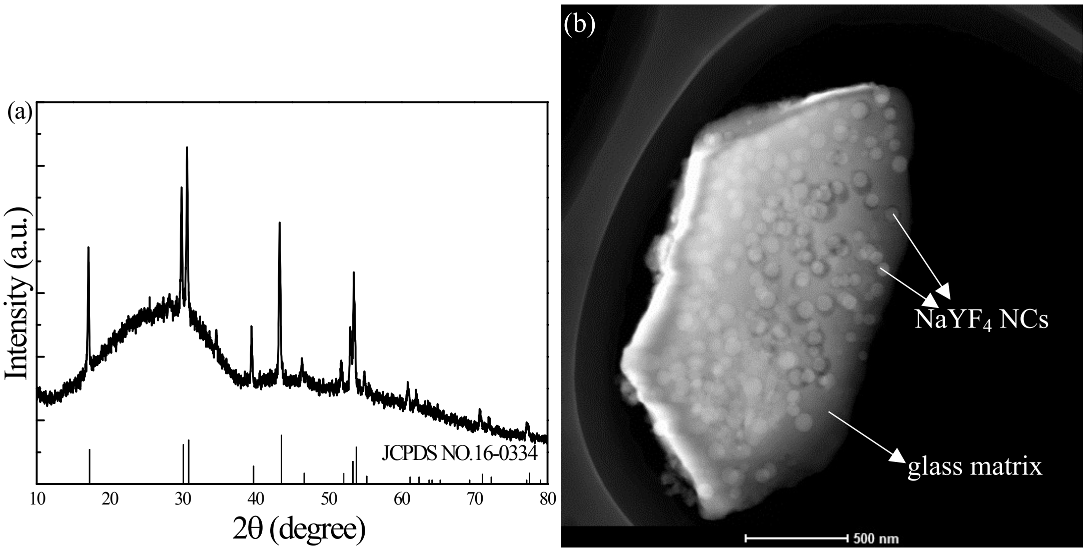

Figure S7 (a) XRD pattern and (b) HAADF-STEM image of Yb/Er: $NaYF_4$@glass sample. Bars represent diffraction data of hexagonal β-$NaYF_4$ crystal (JCPDS No. 16-0334). The precipitated phase inside glass is hexagonal $NaYF_4$, and the particle sizes are in the range of 40~100 nm.

The glass composite for the Yb/Er: $NaYF_4$@glass sample is 55SiO_2-6Al_2O_3-12Na_2O-19NaF-8YF_3. The sample was prepared by melt-quenching and subsequent heat-treatment. About 15 g of high-purity raw materials were mixed and ground evenly, and then placed in an alumina crucible at 1500 ℃ for 30 minutes in the ambient atmosphere. The melt was poured into a pre-heated brass mold at 350 ℃ and then cooled to room temperature to obtain precursor glass. Finally, the Yb/Er: $NaYF_4$@glass was achieved by heating the precursor glass at 650 °C for 2 h to induce β-$NaYF_4$ crystallization.

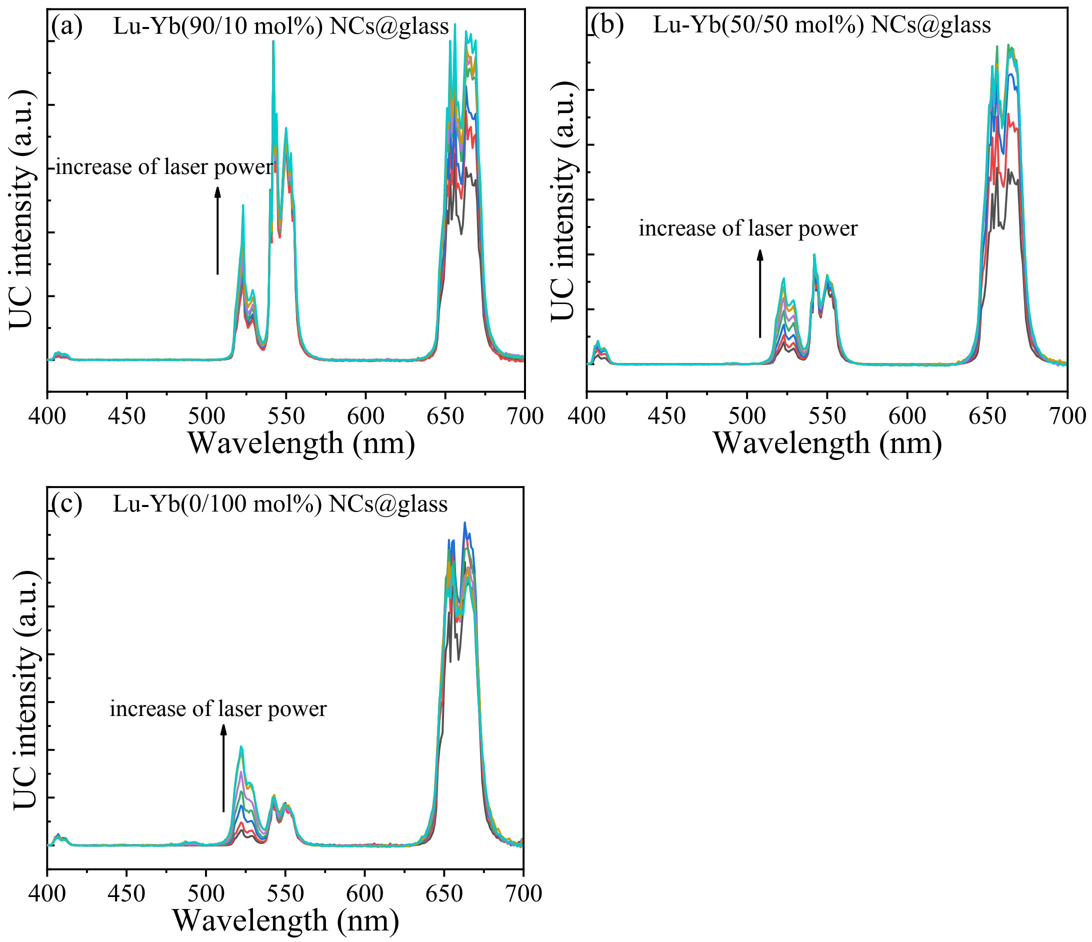

Figure S8 Laser power dependent UC emission spectra of Er: $K(Lu/Yb)_2F_7$ NCs@glass (all the spectra are normalized at Er^{3+} 545 nm emission assigned to $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition): (a) 10 mol% Yb, (b) 50 mol% Yb and (c) 100 mol% Yb.