

Electronic Supporting Information

Glass-Limited Yb/Er: NaLuF₄ Nanocrystals: Reversible Hexagonal-to-Cubic Phase Transition and Anti-Counterfeiting

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Table S1 crystallographic data of cubic α -NaLuF₄ (left) and hexagonal β -NaLuF₄ (right).

Atomic parameters			
Atom	x/a	y/b	z/c
Na	0.0000	0.0000	0.0000
Lu	0.0000	0.0000	0.0000
F	0.2500	0.2500	0.2500
Space-group	a	b	c
Fm-3m	5.47 Å	5.47 Å	5.47 Å

Atomic parameters			
Atom	x/a	y/b	z/c
Na(1)	0.6667	0.3333	0.5000
Na(2)	0.3333	0.6667	0.6890
Lu(1)	0.0000	0.0000	0.0000
Lu(2)	0.6667	0.3333	0.5000
F(1)	0.6460	0.1256	0.0000
F(2)	0.6970	0.7220	0.5000
Space-group	a	b	c
P -6	5.91 Å	5.91 Å	3.50 Å

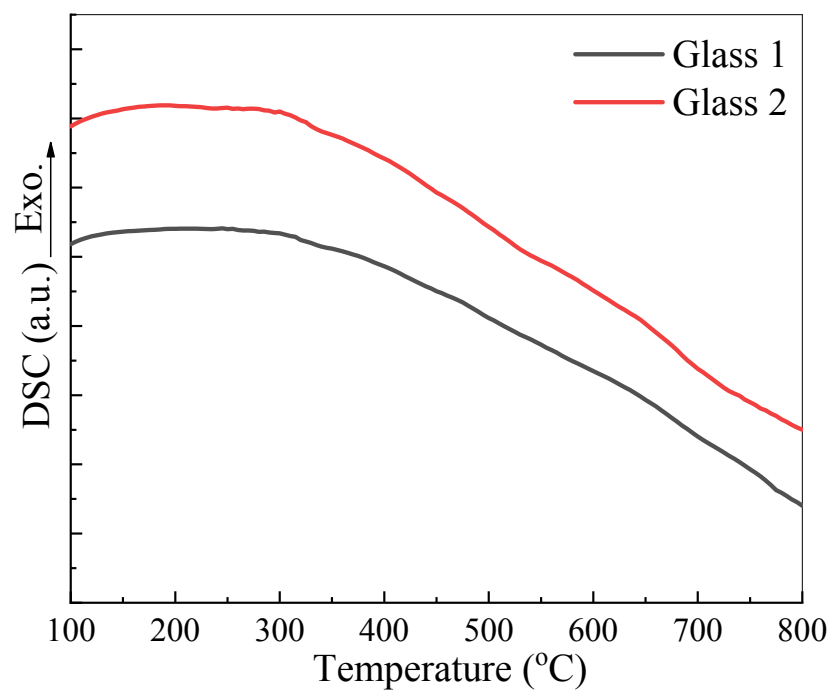


Figure S1 DSC curve of the glass 1 and glass 2 samples recorded at a heating rate of 10 K/min in temperature range of 100~800 °C.

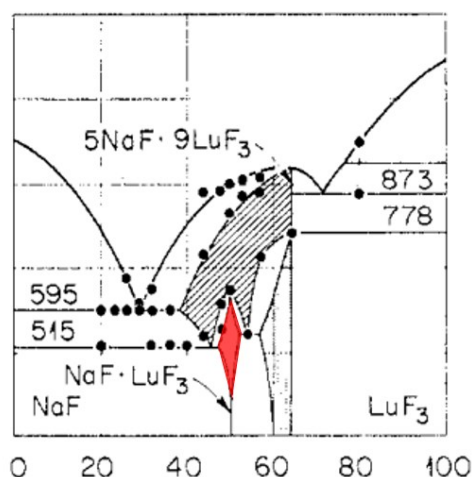


Figure S2 Binary equilibrium phase diagram of the NaF-LuF₃ system ^{S1,S2}, in which the red region represents hexagonal NaF-LuF₃ solid-solution phase.

[S1] Thoma, R. E.; Hebert, G. M.; Insley, H.; Weaver, C. F. Phase Equilibria in the System Sodium Fluoride-Yttrium Fluoride. *Inorg. Chem.* **1963**, 2, 1005-1012.

[S2] Thoma, R. E.; Insley, H.; Hebert, G. M. The Sodium Fluoride-Lanthanide Trifluoride Systems. *Inorg. Chem.* **1966**, 5, 1222-1229.

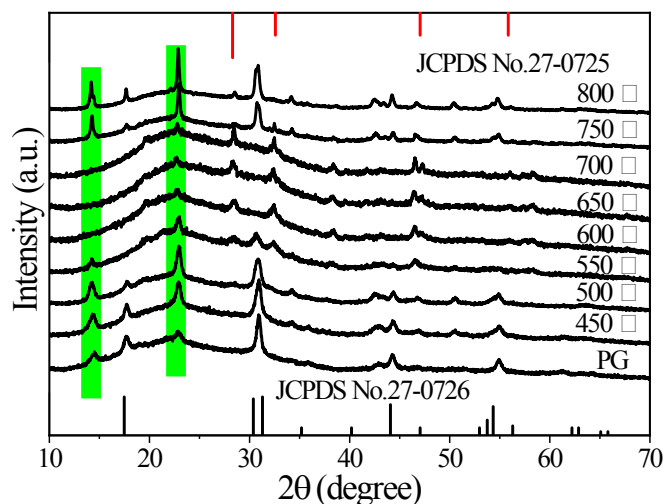


Figure S3 XRD patterns of Eu³⁺-doped precursor glass and NaLuF₄@glass samples obtained by heating PG at different temperatures (450~800 °C). Bars represent standard diffraction data of cubic α-NaLuF₄ (JCPDS No. 27-0725) and hexagonal β-NaLuF₄ (JCPDS No. 27-0726).

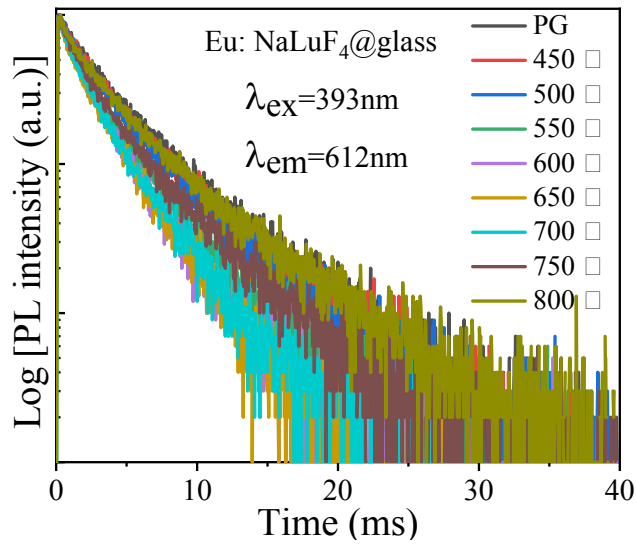


Figure S4 PL decay curves ($\lambda_{em}=612$ nm) of Eu^{3+} -doped precursor glass and NaLuF_4 @glass samples obtained by heating PG at different temperatures (450~800 °C).

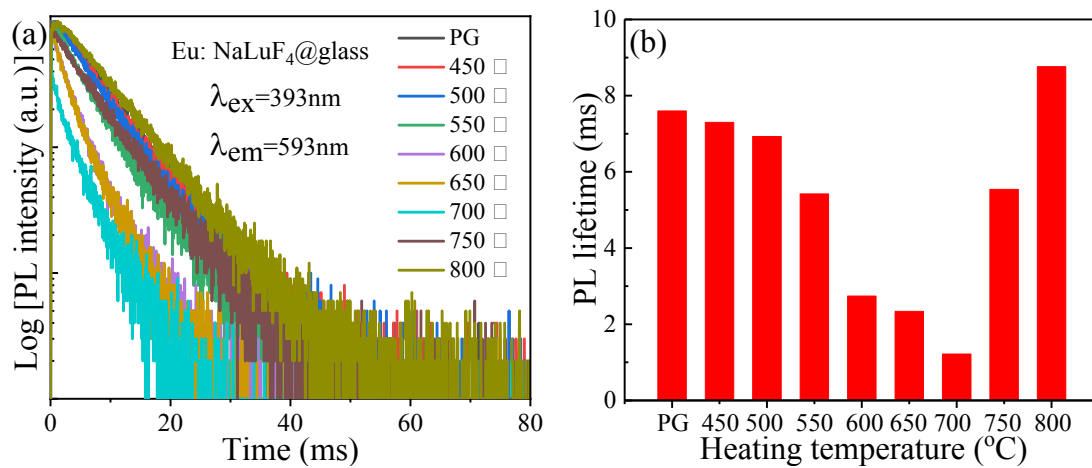


Figure S5 (a) PL decay curves ($\lambda_{em}=593$ nm) of Eu^{3+} -doped precursor glass and NaLuF_4 @glass samples obtained by heating PG at different temperatures (450~800 °C). (b) The evaluated decay lifetime versus heating temperature.

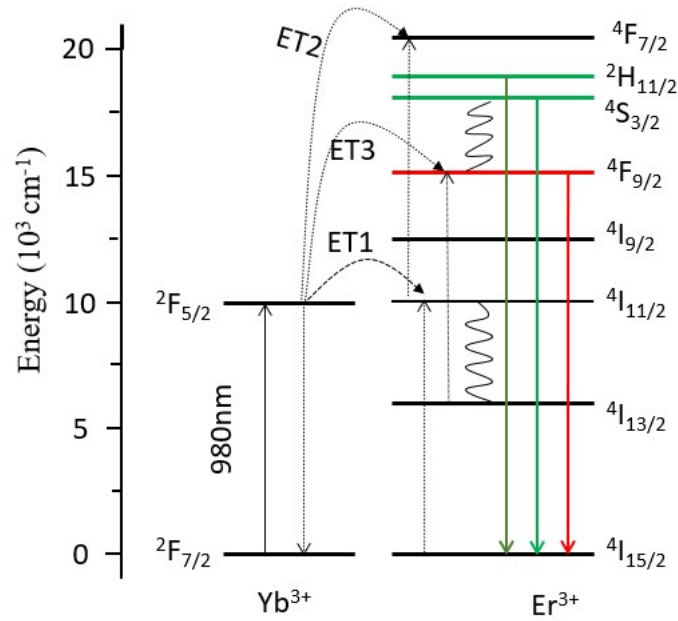


Figure S6 Energy level diagram of Yb³⁺ and Er³⁺ activators, showing possible energy transfer upconversion mechanism in the present Yb/Er: NaLuF₄@glass.

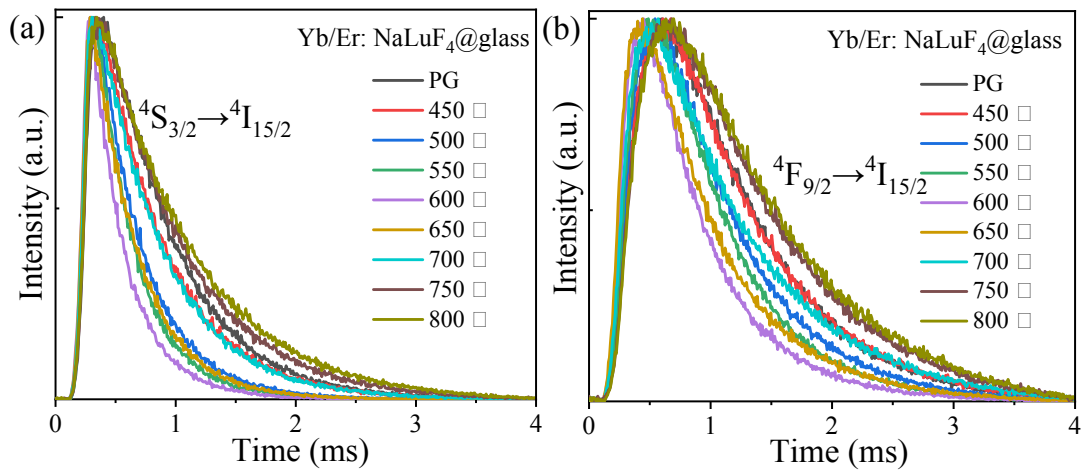


Figure S7 UC decay curves of Yb/Er-doped precursor glass and NaLuF₄@glass samples obtained by heating PG at different temperatures (450~800 °C): (a) monitoring ⁴S_{3/2} 543 nm green emitting, (b) monitoring ⁴F_{9/2} 669 nm red emitting.

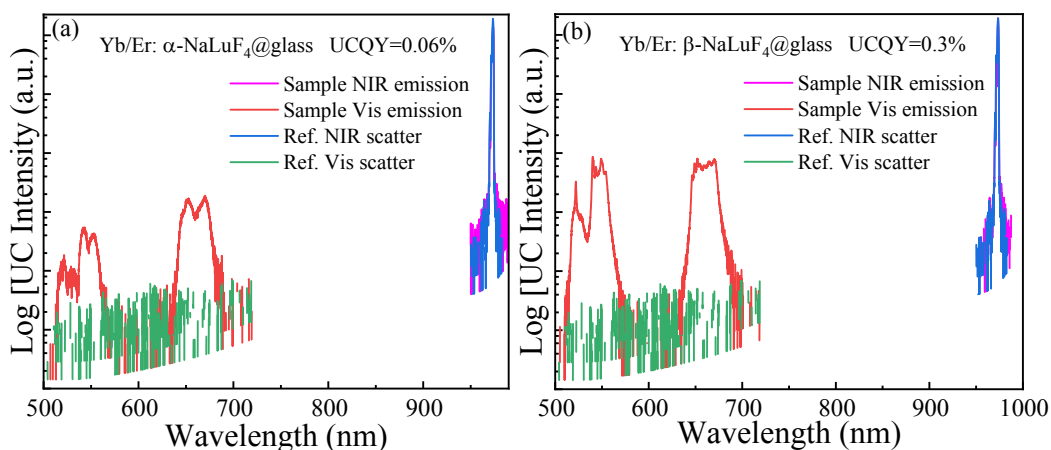


Figure S8 Quantitative UC emission spectra of Yb/Er-doped NaLuF_4 @glass samples and the corresponding references for UCQY determination: (a) α - NaLuF_4 , (b) β - NaLuF_4 . All the spectra were recorded by a spectrofluorometer equipped with an integrating sphere.

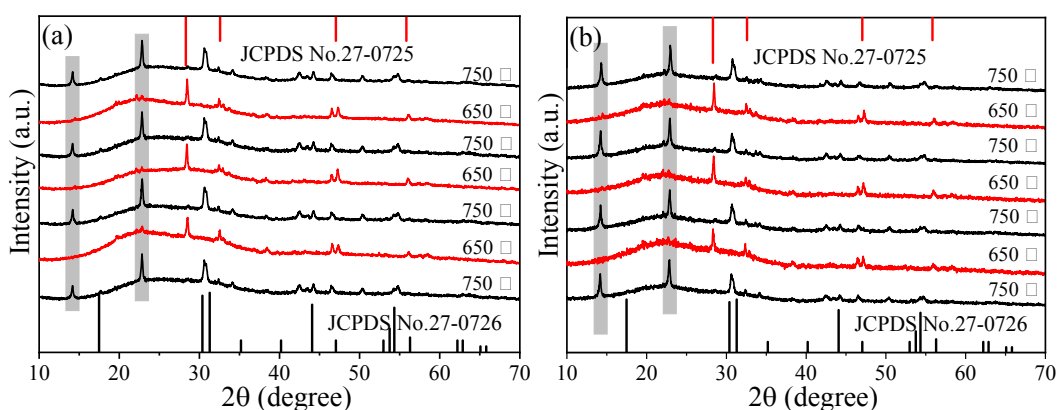


Figure S9 XRD patterns of Yb/Er ($x/1$ mol%) doped NaLuF_4 @glass samples obtained by 750 °C / 650 °C cycling heat-treatment: (a) $x=50$, (b) $x=80$. Bars represent standard diffraction data of cubic α - NaLuF_4 (JCPDS No. 27-0725) and hexagonal β - NaLuF_4 (JCPDS No. 27-0726).

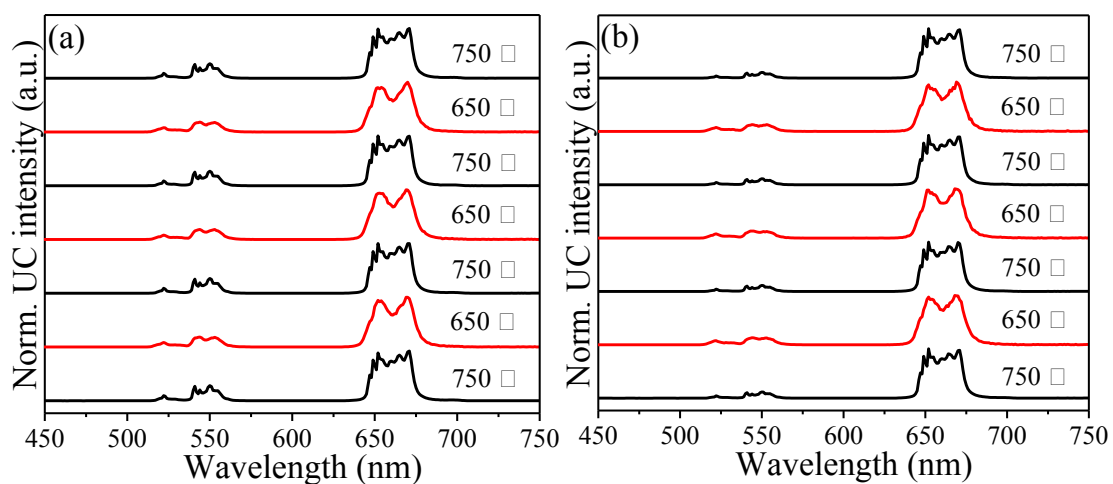


Figure S10 UC emission spectra Yb/Er (x/1 mol%) doped NaLuF₄@glass samples obtained by 750 °C / 650 °C cycling heat-treatment: (a) x=50, (b) x=80. The laser excitation wavelength is 980 nm.

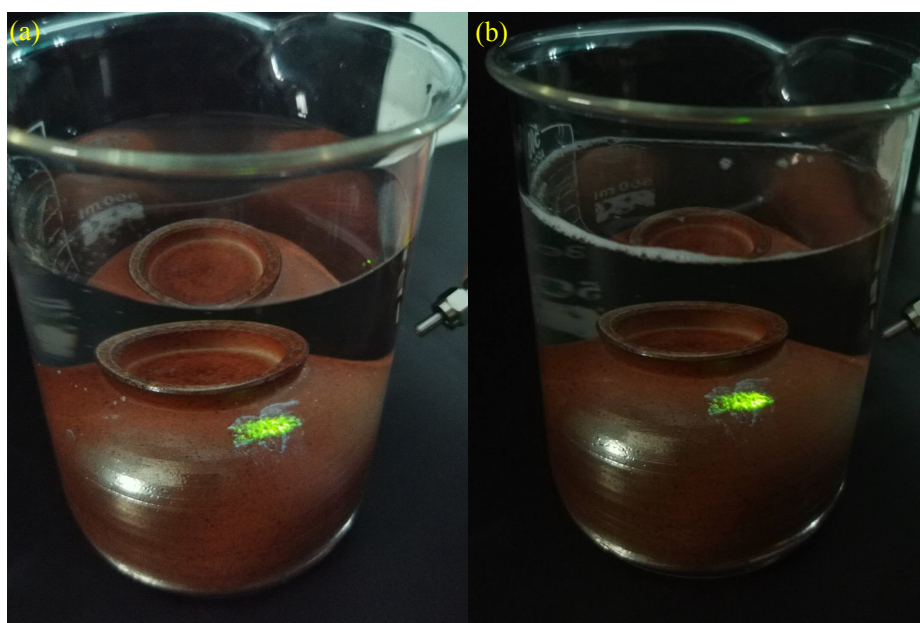


Figure S11 UC luminescence photographs of the flower pattern decorated porcelain in solution for 180 days: (a) water solution, (b) oil solution. The incident laser wavelength is 980 nm.