Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Structural confinement toward suppressing concentration and thermal quenching for improving near-infrared luminescence of Fe^{3+}

Fangyi Zhao, Yuhe Shao, Zhen Song* and Quanlin Liu*

The Beijing Municipal Key Laboratory of New Energy Materials and Technologies, School of Materials Sciences and Engineering, University of Science and Technology Beijing, Beijing 100083, China. E-mail: zsong@ustb.edu.cn; qlliu@ustb.edu.cn

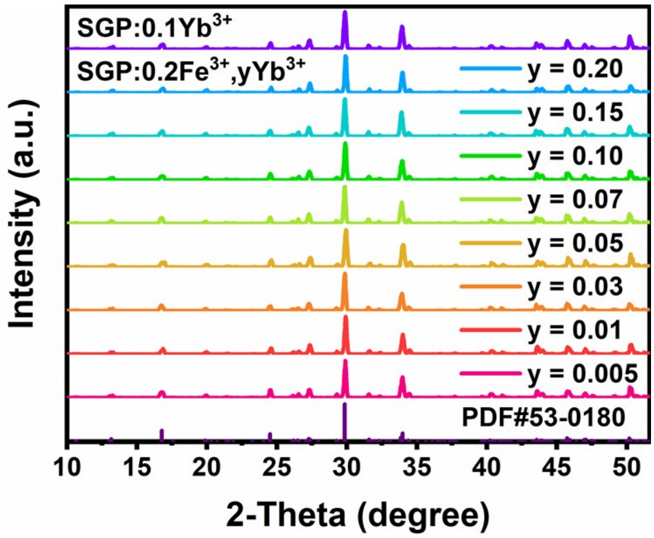

Fig. S1 XRD patterns of SGP:0.2Fe^{3+},$y$$Yb^{3+}$ ($0.005 \leq y \leq 0.20$) and SGP:0.1Yb^{3+}.

Table S1. Main parameters of processing and refinement of SGP:0.2Fe^{3+} and $Sr_9Fe(PO_4)_7$ samples

Compound	SGP:0.2Fe^{3+}	$Sr_9Fe(PO_4)_7$
Space Group	*I*12/*a*1	*I*12/*a*1
Symmetry	Monoclinic	Monoclinic
a (Å)	17.9674(9)	17.9749(8)
b (Å)	10.5955(5)	10.6087(5)
c (Å)	18.2615(8)	18.2795(8)
$\alpha = \gamma$ (°)	90.00	90.00
β (°)	132.778(2)	132.843(2)
V (Å^3)	2551.7(2)	2555.8(2)
R_p (%)	12.6	14.8
R_{wp} (%)	16.0	19.4
R_{exp} (%)	10.03	11.20
χ^2	2.54	3.01

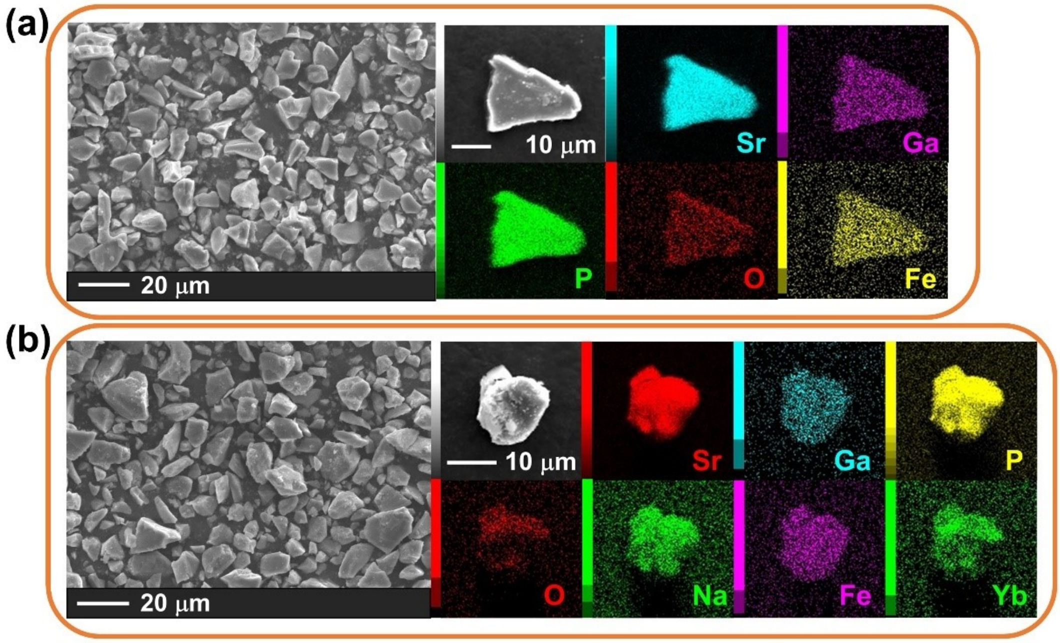

Fig. S2 SEM images and element mapping images of SGP:0.2Fe^{3+} and SGP:0.2Fe^{3+},0.07Yb^{3+}.

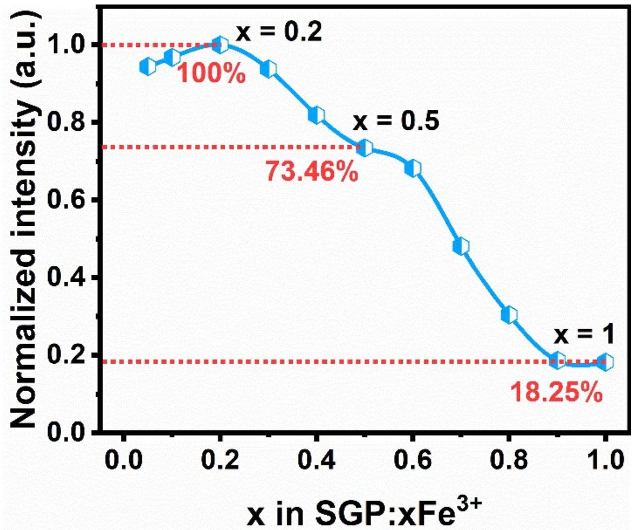

Fig. S3 Relationship between integrated PL intensity and Fe^{3+} concentration in SGP:$x$$Fe^{3+}$.

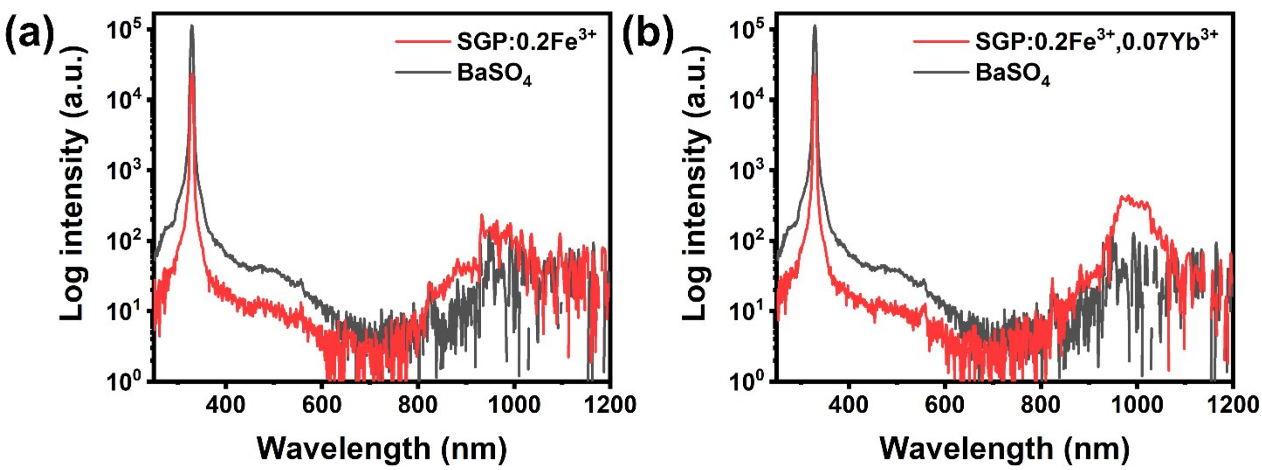

Fig. S4 (a) Spectra of SGP:0.2Fe^{3+} and $BaSO_4$ to determine the IQE and EQE values. (b) Spectra of SGP:0.2Fe^{3+},0.07Yb^{3+} and $BaSO_4$ to determine the IQE and EQE values.

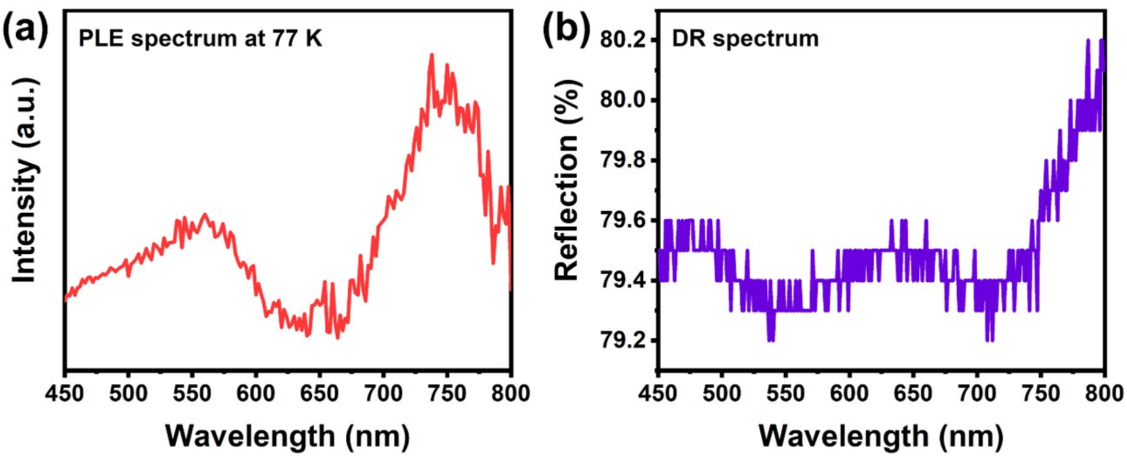

Fig. S5 Magnified (a) PLE spectrum measured at 77 K and (b) DR spectrum ranging from 450 to 800 nm of SGP:0.2Fe^{3+}.

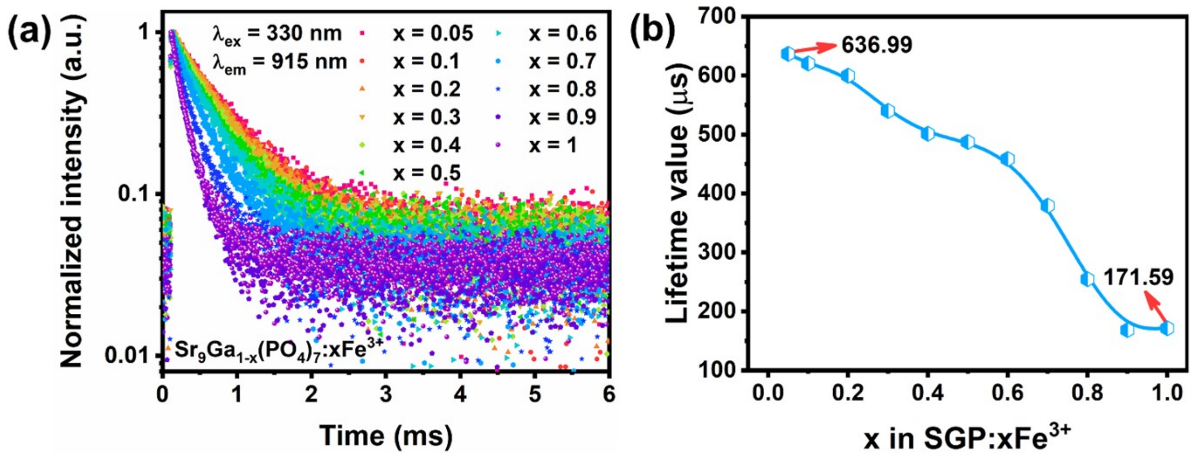

Fig. S6 (a) Luminescence decay curves of SGP:$x$$Fe^{3+}$ ($0.05 \leq x \leq 1$) excited by 330 nm and monitoring at 915 nm. (b) Relationship between lifetime values and Fe^{3+} concentration in SGP:$x$$Fe^{3+}$.

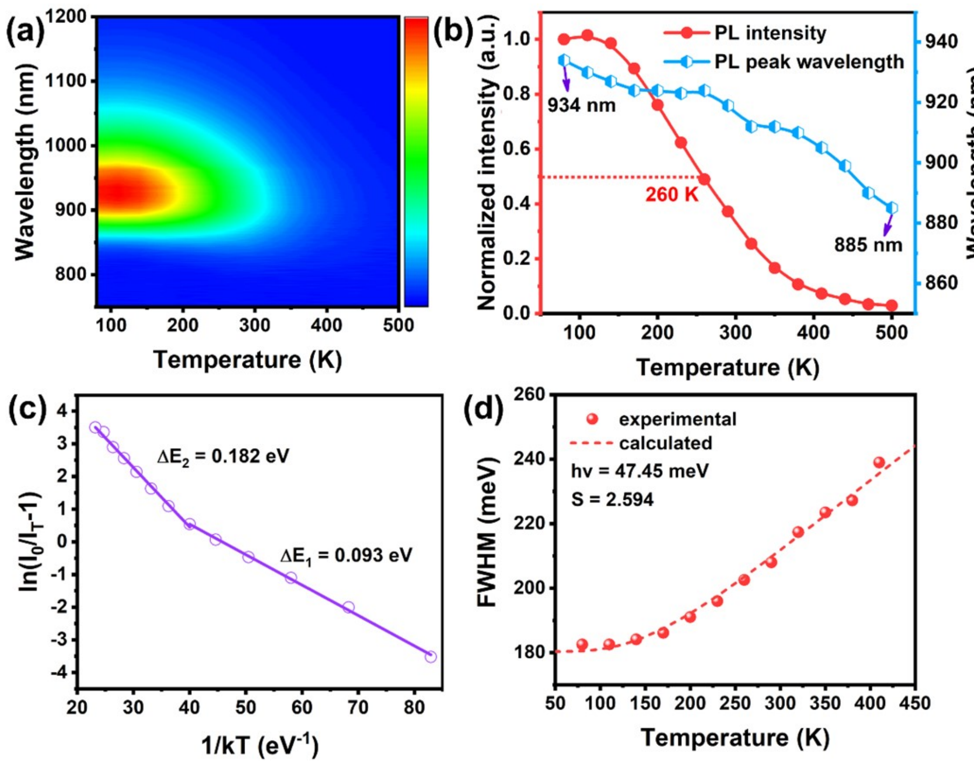

Fig. S7 (a) Temperature-dependent PL spectra at 80-500 K, (b) dependence of PL intensity and PL peak wavelength on temperature, (c) activation energy plots using the Arrhenius equation, (d) fitting of the FWHM as a function of temperature for SGP:0.2Fe^{3+}.

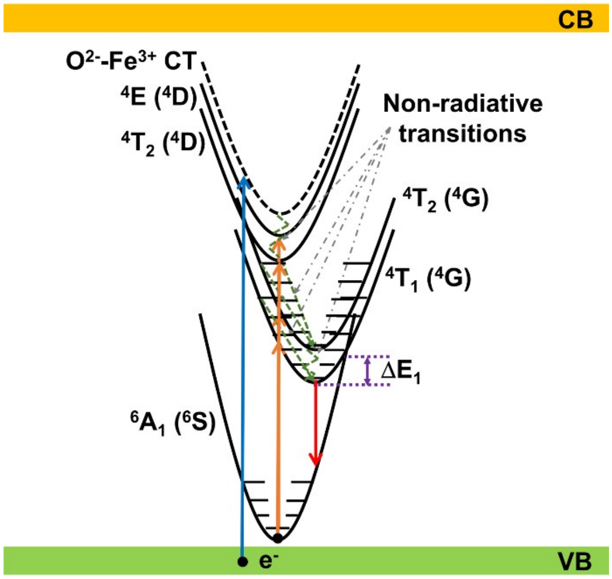

Fig. S8 Configurational coordinate diagram to illustrate thermal quenching behavior.

The temperature-dependence of PL intensity can be described by a modified Arrhenius equation:[1]

$$I_T = \frac{I_0}{1 + A\exp(-\Delta E / kT)} \qquad \text{(S1)}$$

where I_0 is the initial intensity, I_T is the intensity at a given temperature, A is a constant, k is the Boltzmann constant and ΔE is the activation energy for the thermal quenching.

The widening of FWHM can be explained qualitatively based on the following Equation:[2]

$$FWHM = 2.36 \times h\nu \times \sqrt{S} \times \sqrt{\coth(\frac{h\nu}{2kT})} \qquad \text{(S2)}$$

where $h\nu$, S, k and T represent the energy of lattice vibration, Huang-Rhys parameter, Boltzmann constant and Kelvin temperature, respectively.

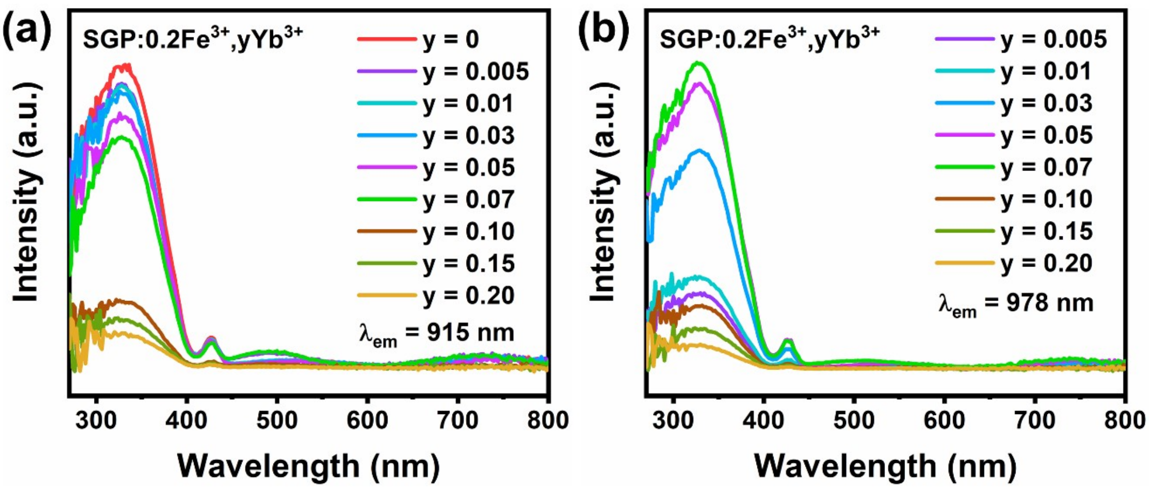

Fig. S9 (a) PLE spectra of SGP:0.2Fe^{3+},$y$$Yb^{3+}$ ($0 \le y \le 0.20$) monitoring at 915 nm. (b) PLE spectra of SGP:0.2Fe^{3+},$y$$Yb^{3+}$ ($0.005 \le y \le 0.20$) monitoring at 978 nm.

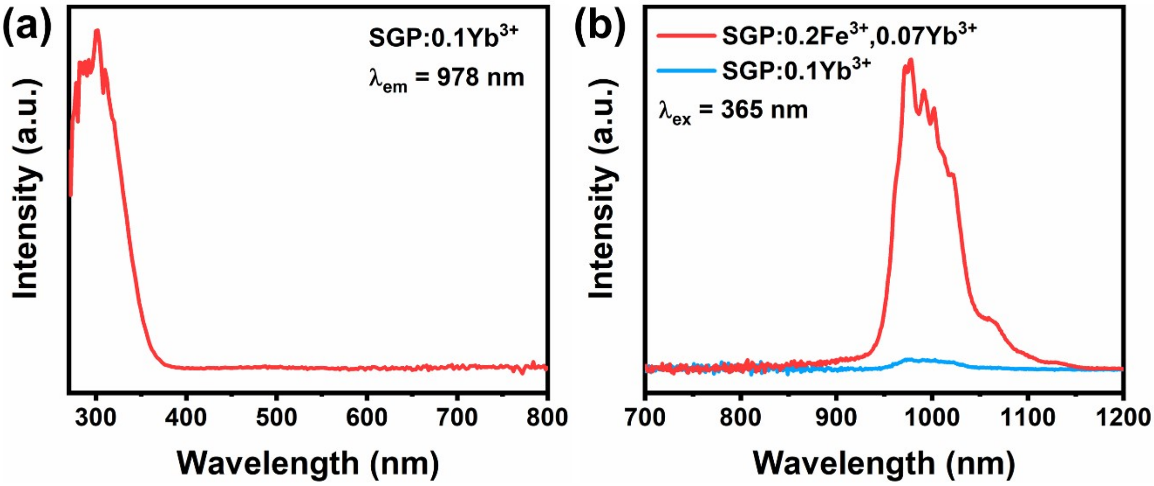

Fig. S10 (a) PLE spectrum of $SGP:0.1Yb^{3+}$ monitoring at 978 nm. (b) PL spectra of $SGP:0.1Yb^{3+}$ and $SGP:0.2Fe^{3+},0.07Yb^{3+}$ excited by 365 nm.

The ET efficiency (η_{ET}) can be calculated by the attenuation of lifetime based on the following equation:[3]

$$\eta_{ET} = 1 - \frac{\tau_{Fe}}{\tau_{Fe_0}} \qquad \text{(S3)}$$

where τ_{Fe} is the lifetime of Fe^{3+} in Yb^{3+}-doped samples, and τ_{Fe0} represents the lifetime of Fe^{3+} in Yb^{3+}-free samples.

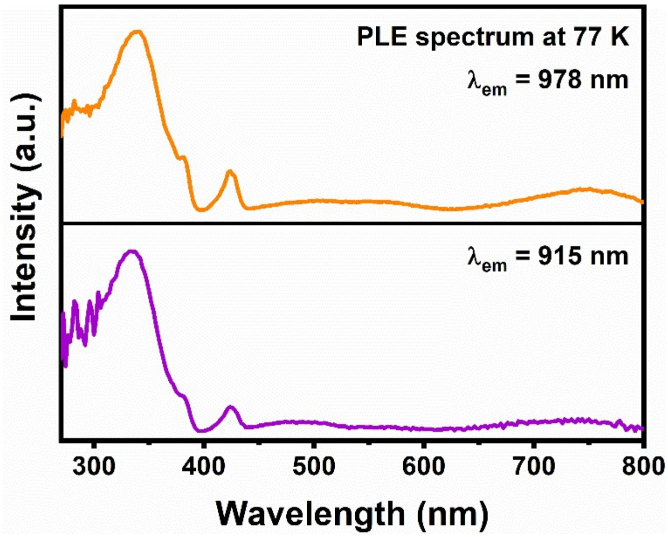

Fig. S11 PLE spectra of $SGP:0.2Fe^{3+},0.07Yb^{3+}$ monitoring at 915 and 978 nm measured at 77 K.

References

1 Q. Y. Shao, H. Ding, L. Q. Yao, J. F. Xu, C. Liang and J. Q. Jiang, Photoluminescence properties of a $ScBO_3:Cr^{3+}$ phosphor and its applications for broadband near-infrared LEDs, *RSC Adv.*, 2018, **8**, 12035–12042.

2 X.-D. Wei, L.-Y. Cai, F.-C. Lu, X.-L. Chen, X.-Y. Chen and Q.-L. Liu, Structure and luminescence of $Ca_2Si_5N_8:Eu^{2+}$ phosphor for warm white light-emitting diodes, *Chinese Phys. B*, 2009, **18**, 3555–3562.

3 P. I. Paulose, G. Jose, V. Thomas, N. V. Unnikrishnan and M. K. R. Warrier, Sensitized fluorescence of Ce^{3+}/Mn^{2+} system in phosphate glass, *J. Phys. Chem. Solids*, 2003, **64**, 841–846.