Tunable emission of $Li_4SrCaSi_2O_{4-y}N_{2y/3}$: Eu^{2+} phosphors based on anion substitution induction for WLEDs and optical thermometry

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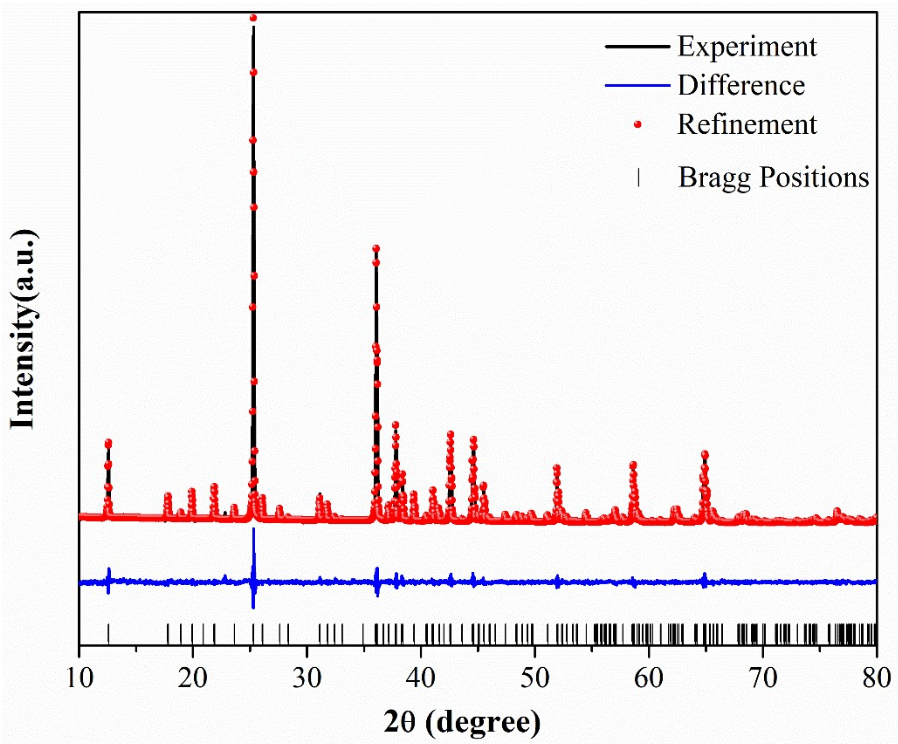

Figure S1 Rietveld refinement XRD patterns of $Li_4SrCaSi_2O_4N_{8/3}$ (experiment: black line, difference: blue line, refinement: red ball and Bragg positions: black tick marks)

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Table S1 The refinement data and fractional atomic coordinates of $Li_4SrCaSi_2O_4N_{8/3}$

Space group：Pbcm (57) (orthorhombic)	
Cell parameter	**Reliability Factors**
Crystal Density (g/cm^3)=9.005	R_{exp}(%)=4.63
Z=4	R_{wp}(%)=6.17
a =4.98487 Å	R_p(%)=5.32
b =9.93483 Å	*GOF*=1.41
c =14.0471 Å	
V =696.9828 Å^3	

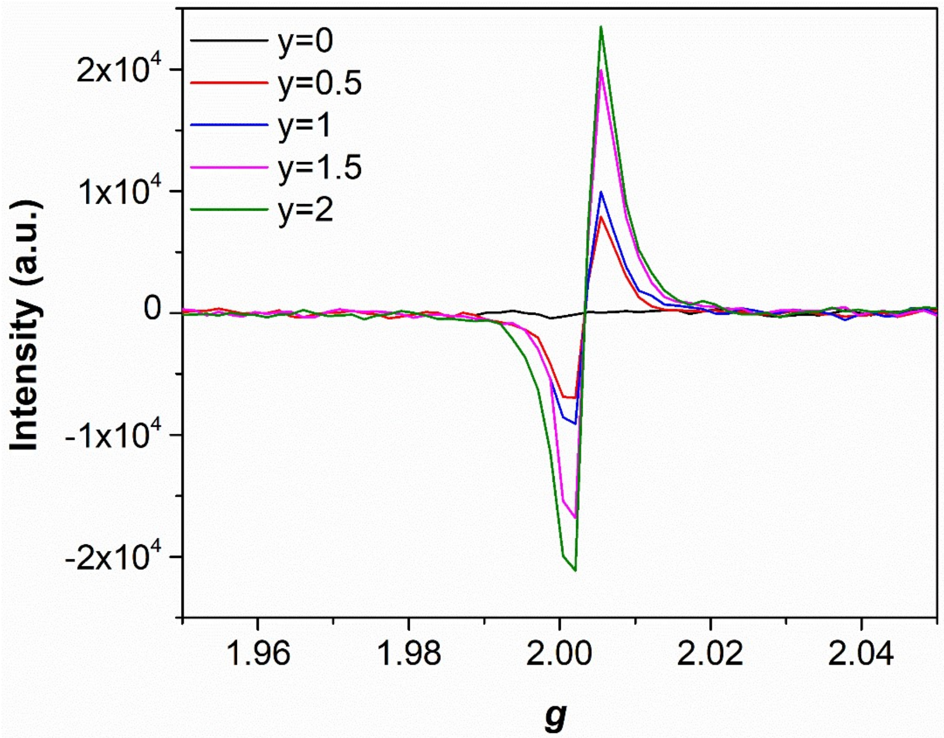

Figure S2 EPR signals of $Li_4SrCaSi_2O_{8-2y}N_{4y/3}$ (y=0, 0.5, 1, 1.5 and 2) (test temperature is 77K)

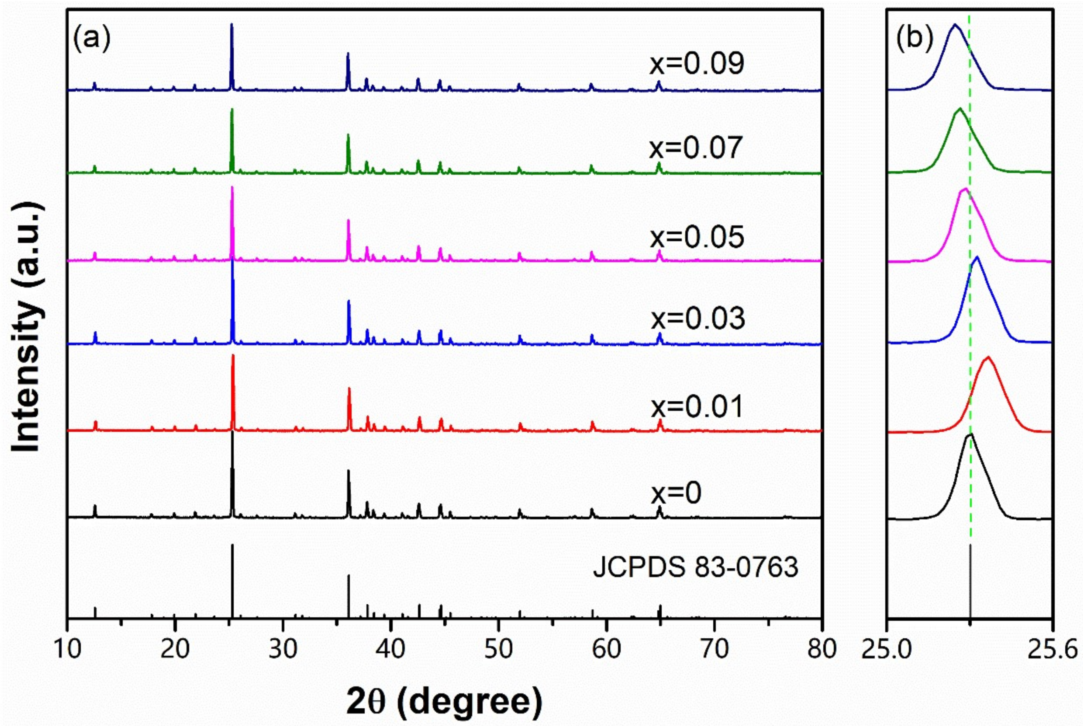

Figure S3 (a) XRD patterns; bars at bottom present the standard data of orthorhombic $Li_4SrCa(SiO_4)_2$ (PDF 83-0763), (b) Partially enlarged XRD patterns of the series of $Li_4SrCaSi_2O_4N_{8/3}$: xEu^{2+} samples with different Eu^{2+} content.

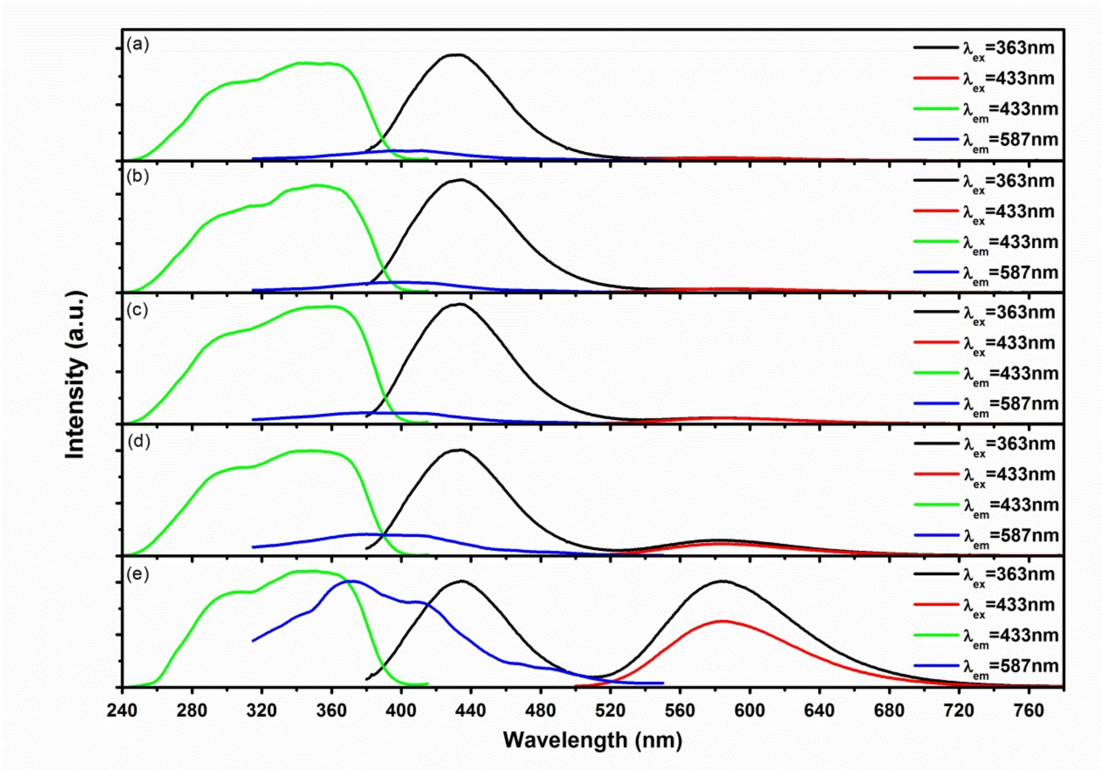

Figure S4 The excitation and emission spectra of the series of $Li_4SrCaSi_2O_{8-2y}N_{4y/3}$: $0.05Eu^{2+}$ samples with different N^{3-} content (a) y=0, (b) y=0.5, (c) y=1, (d) y=1.5 and (e) y=2.

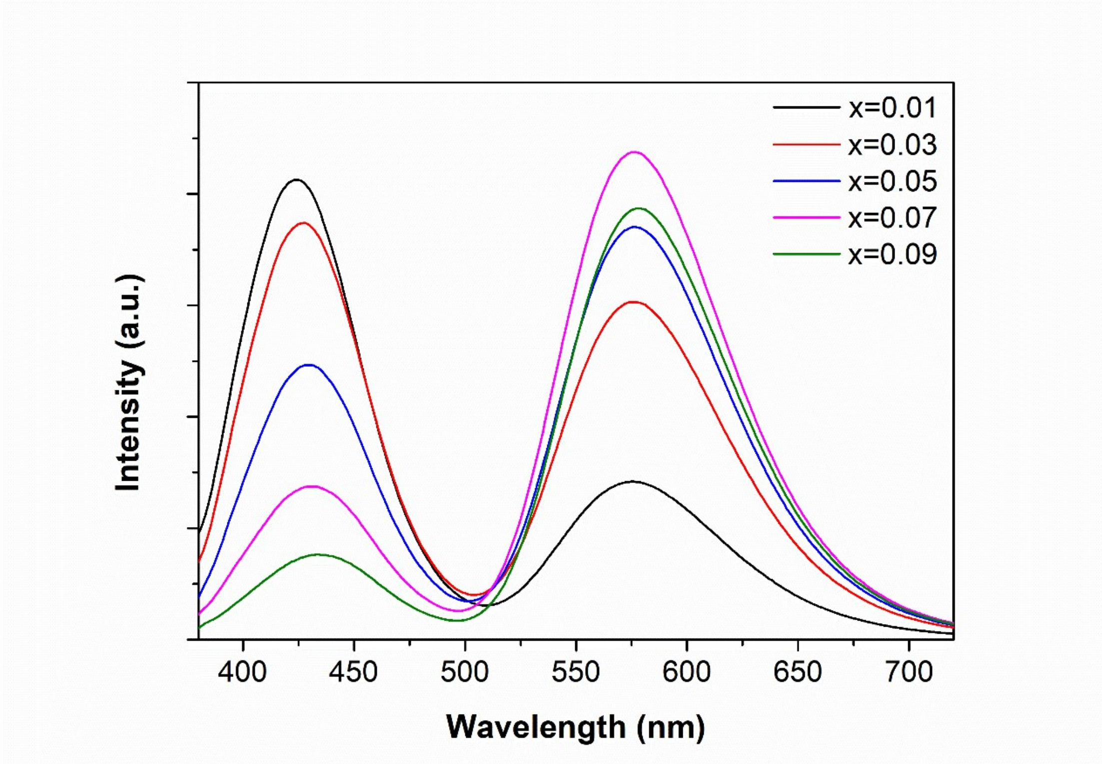

Figure S5 The emission spectra of the series of $Li_4SrCaSi_2O_4N_{8/3}$: xEu^{2+} samples (x=0.01, 0.03, 0.05, 0.07 and 0.09)

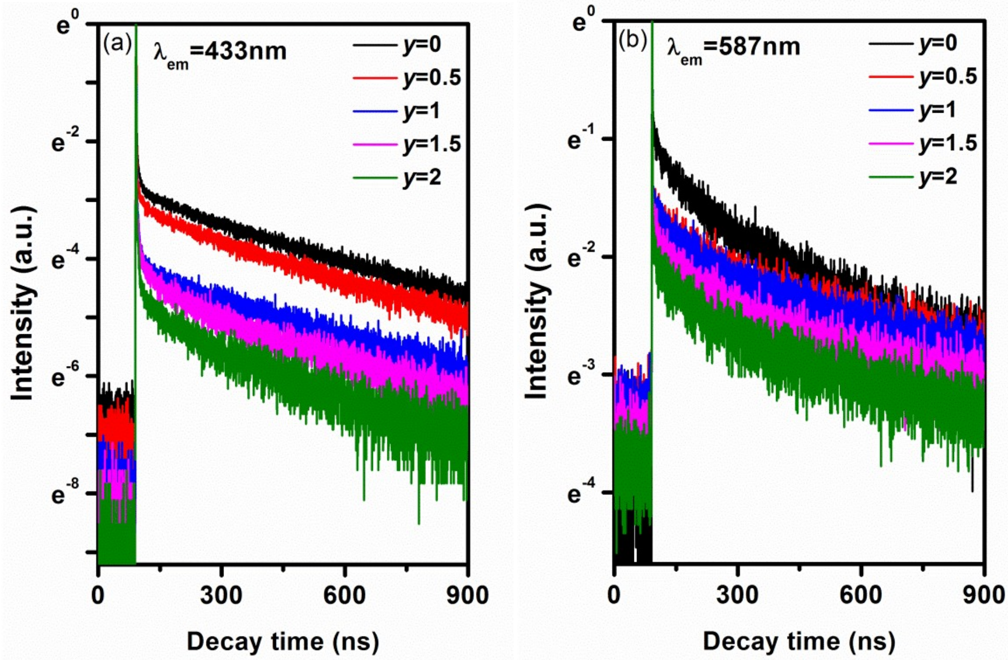

Figure S6 The decay curves of $Li_4SrCaSi_2O_{8-2y}N_{4y/3}$: $0.05Eu^{2+}$ (y=0, 0.5, 1, 1.5 and 2) samples with the excitation at 370 nm and monitored at (a) 433 nm and (b) 587nm

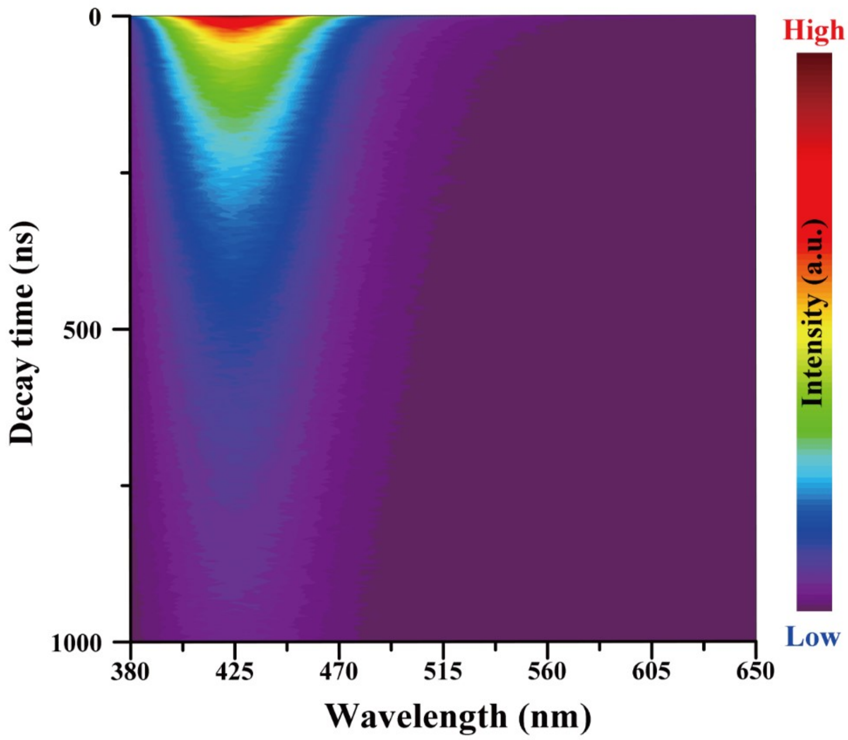

Fig. S6 (c) Time-resolved emission spectra (TRES) of $Li_4SrCa(SiO_4)_2$: $0.05Eu^{2+}$ under 370 nm excitation at room temperature

The decay curves of $Li_4SrCaSi_2O_{8-2y}N_{4y/3}$: $0.05Eu^{2+}$ (y=0, 0.5, 1, 1.5 and 2) samples with the excitation at 370 nm and monitored at 433 nm and 587nm have been shown in Figure S6. It is obvious that the curves can be well fitted by a second-order exponential curve by the biexponential formula:

$$I(t) = A + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \qquad \text{(S1)}$$

where I is the luminescent intensity, A_1 and A_2 are fitting constants, t is the time, τ_1 and τ_2 are short and long lifetimes for exponential components, respectively. Therefore, the average lifetimes (τ^*) of $Li_4SrCaSi_2O_{8-2y}N_{4y/3}$: $0.05Eu^{2+}$ (y=0, 0.5, 1, 1.5 and 2) samples can be calculated by the following formula:

$$\tau^* = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \qquad \text{(S2)}$$

and the related parameters and average lifetime values listed in Table S2.

Table S2 the related parameters and average lifetime values

	433nm					587nm				
	A_1	τ_1	A_2	τ_2	τ^*(ns)	A_1	τ_1	A_2	τ_2	τ^*(ns)
y=0	0.50	5.03	0.36	329.60	322.80	0.21	22.79	0.47	272.51	263.37
y=0.5	0.40	6.01	0.42	306.50	300.97	0.23	48.67	0.48	434.29	414.57
y=1	0.60	3.96	0.18	304.72	292.36	0.25	39.07	0.45	364.58	346.53
y=1.5	0.58	4.64	0.20	208.59	196.02	0.23	22.55	0.42	280.76	269.86
y=2	0.64	3.42	0.15	191.44	178.28	0.23	18.55	0.40	279.23	269.83

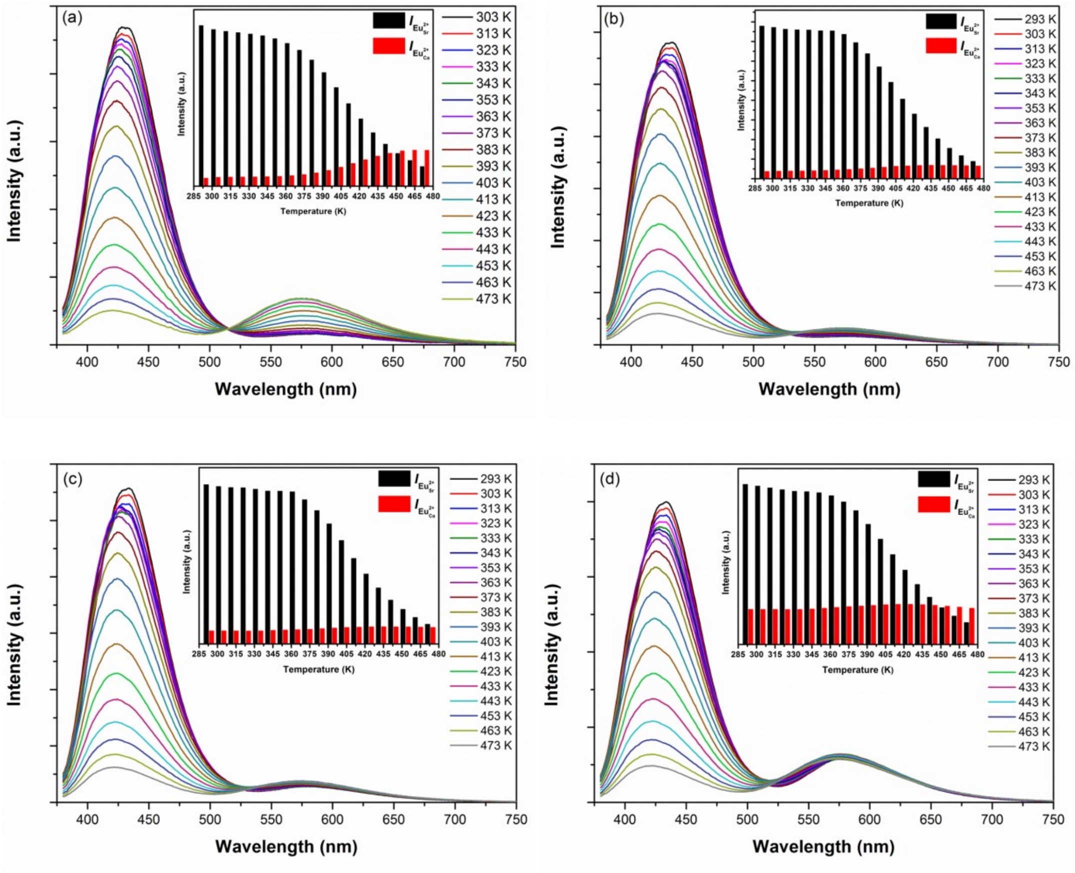

Figure S7 The temperature-dependent (273 ~ 473 K) photoluminescence spectra of $Li_4SrCaSi_2O_{8-2y}N_{4y/3}$: $0.05Eu^{2+}$ phosphors, (a) y=0, (b) y=0.5, (c) y=1 and (d) y=1.5; the inset shows the Histogram displaying the integrated emission intensity of Eu_{Sr}^{2+} and Eu_{Ca}^{2+} at various temperatures

Exhaustive inference for Equation (1):

The fluorescence lifetime follows the classical Mott–Seitz model which describes the total transition probability of an emitting level by the sum of radiative and nonradiative transition probabilities (A_R and A_{NR}, respectively). This can be evaluated by the inverse of the lifetime τ of the emitting level:

$$\frac{1}{\tau}=\frac{1}{\tau_R}+\frac{1}{\tau_{NR}} \quad \text{(S3)}$$

where τ_R is the radiative lifetime (assumed to be temperature independent and equal to τ_0, the lifetime intensity at T=0 K) and τ_{NR} is the nonradiative lifetime that is described by the Arrhenius dependence: $\tau_{NR}=\tau_{NR}(0)\exp(-\Delta E/k_B T)$ where τ_{NR} stands for the nonradiative decay time at T=0 K and ΔE for the activation energy of the thermal quenching process, k_B is the Boltzmann constant. Solving Eq. (3), we can write:

$$\tau=\frac{\tau_0}{1+\alpha exp(-\Delta E/k_B T)} \quad \text{(S4)}$$

where $\alpha=A_{NR}/A_R$. When more than one quenching process is present, the above expression should be generalized including the deactivation though all the channels:

$$\tau=\frac{\tau_0}{1+\sum_i \alpha_i exp(-\Delta E_i/k_B T)} \quad \text{(S5)}$$

The integrated luminescence intensity, I, may be related with τ as:

$$\frac{I_T}{I_0}=\frac{\tau}{\tau_0} \quad \text{(S6)}$$

where I_0 is the emission intensity at T=0 K. Combining Eqs. (5) and (6) it follows:

$$I=\frac{I_0}{1+\sum_i \alpha_i exp(-\Delta E_i/k_B T)} \quad \text{(S7)}$$

Here, the value of activation energy (ΔE_i) is a key parameter of thermal quenching effect, which is the quenching activation energy from the intersection of the excited state and the ground state to the bottom of the excited state.

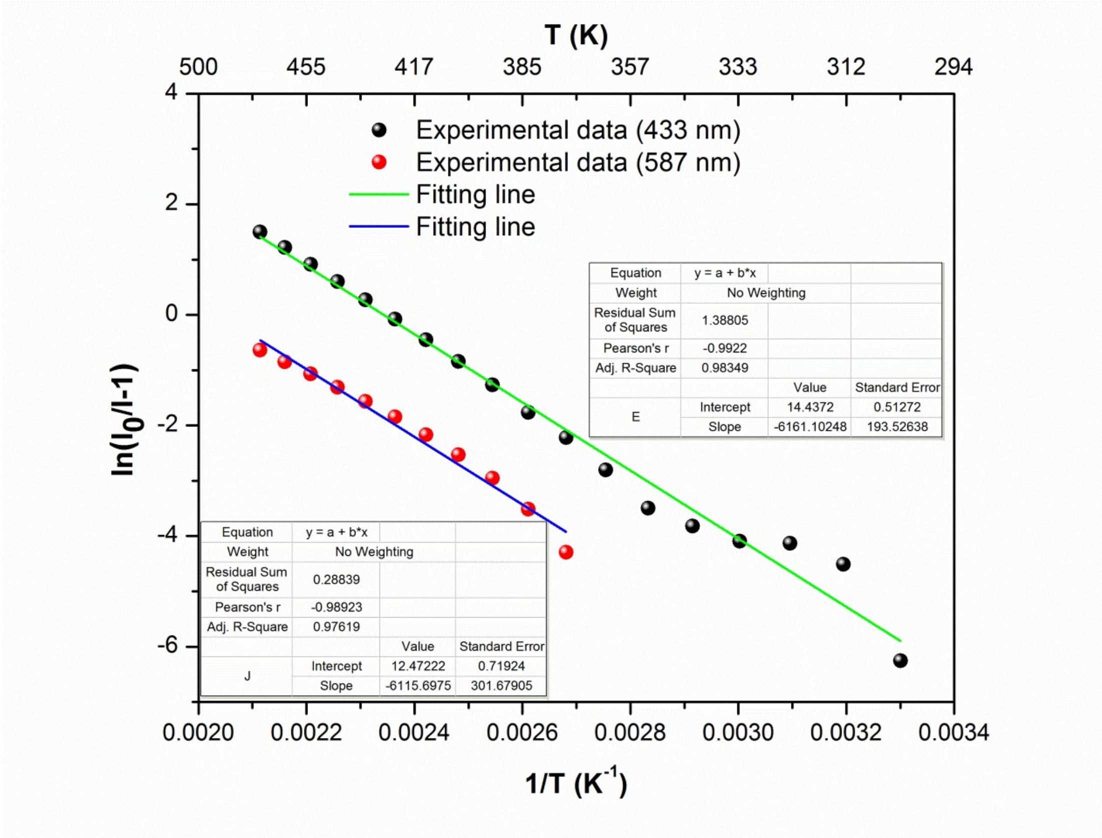

Figure S8 the ln(I_0/I-1) *vs* 1/T lines for two emission bands centered at 433 and 587nm in $Li_4SrCaSi_2O_4N_{8/3}$: Eu^{2+} phosphor

Exhaustive inference for Equation (2):

The relationship between the temperature (T) and the total population of particles in the excited state is as follows:

$$N_T = N_1 + N_2 = \frac{N_0}{1+Aexp(-\Delta E_1/k_BT)} \qquad \text{(S3)}$$

where N_0 is the total population at 0 K, N_1 and N_2 are the population at the excited states Eu_{Ca}^{2+} and Eu_{Sr}^{2+}, respectively, A is a pre-exponential constant, and ΔE_1 is the quenching activation energy, which is the energy difference between the bottom of the excited state Eu_{Ca}^{2+} (***b***) and the intersection (***d***) with the ground state. According to the above analysis, the thermally induced relaxation from the excited state Eu_{Sr}^{2+} to Eu_{Ca}^{2+} is through the paths ***a*** → ***c*** → ***b*** → ***d***, then the total population of the excited state Eu_{Sr}^{2+} can be expressed as follows:

$$N_2 = \left[\frac{B_1}{1+A'exp(-\Delta E_0/k_BT)}\right]\left[\frac{N_0}{1+Aexp(-\Delta E_1/k_BT)}\right] \qquad \text{(S4)}$$

where B_1 is related to the distribution probability from the excited state Eu_{Sr}^{2+} to Eu_{Ca}^{2+}, A' is the exponential pre-constant of the excited state Eu_{Sr}^{2+}, and ΔE_0 is the quenching activation energy, which represents the distance from the bottom of the excited state Eu_{Sr}^{2+} (***a***) to the intersection (***c***) with the excited state Eu_{Ca}^{2+}. For the excited state Eu_{Ca}^{2+}, the population can be expressed as:

$$N_1 = N_T - N_2 = \left[1-\frac{B_1}{1+A'exp(-\Delta E_0/k_BT)}\right]\left[\frac{N_0}{1+Aexp(-\Delta E_1/k_BT)}\right] \qquad \text{(S5)}$$

According to the above equations, the FIR parameter can be derived from the following equation:

$$FIR = \frac{I_{Eu_{Ca}^{2+}}}{I_{Eu_{Sr}^{2+}}} = \frac{N_1}{N_2} = \frac{1-B_1+A'exp\left(-\Delta E_0/k_BT\right)}{B_1} = D + Cexp\left(-\Delta E_0/k_BT\right) \qquad \text{(S6)}$$

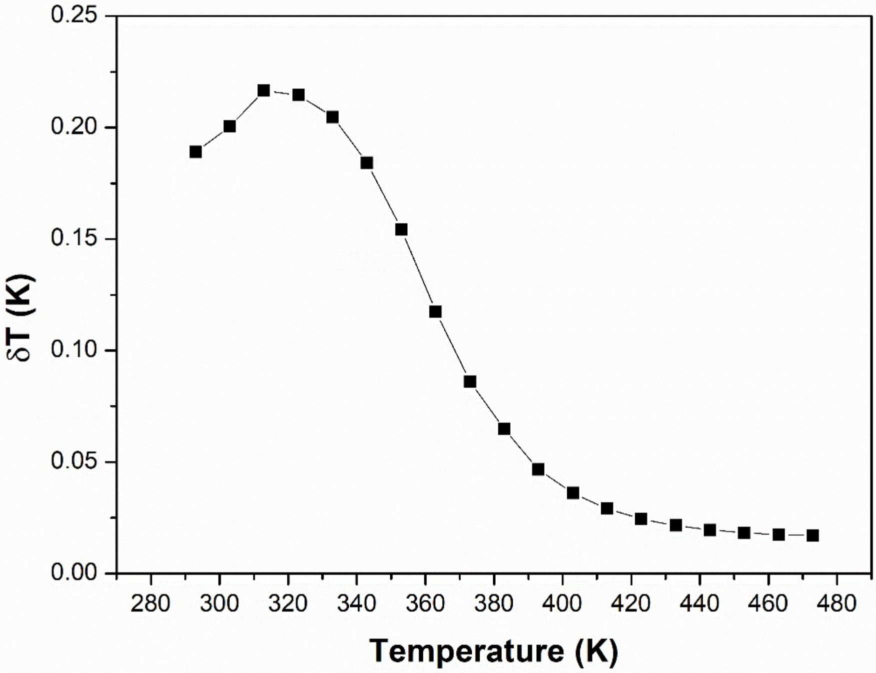

Figure S9 Temperature resolution δT in the temperature range from 293 to 473 K

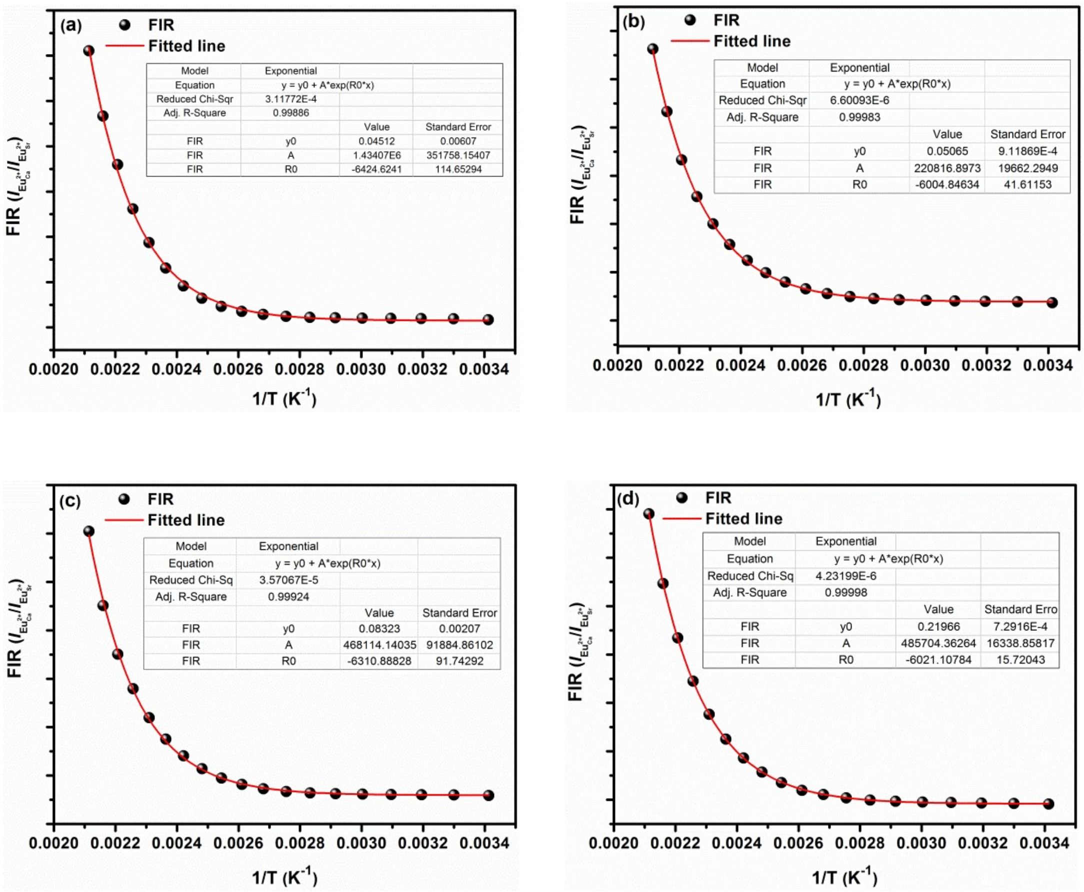

Figure S10 The FIR at different temperatures and the fitted results of $Li_4SrCaSi_2O_{8-2y}N_{4y/3}$: $0.05Eu^{2+}$ phosphors, (a) y=0, (b) y=0.5, (c) y=1 and (d) y=1.5.

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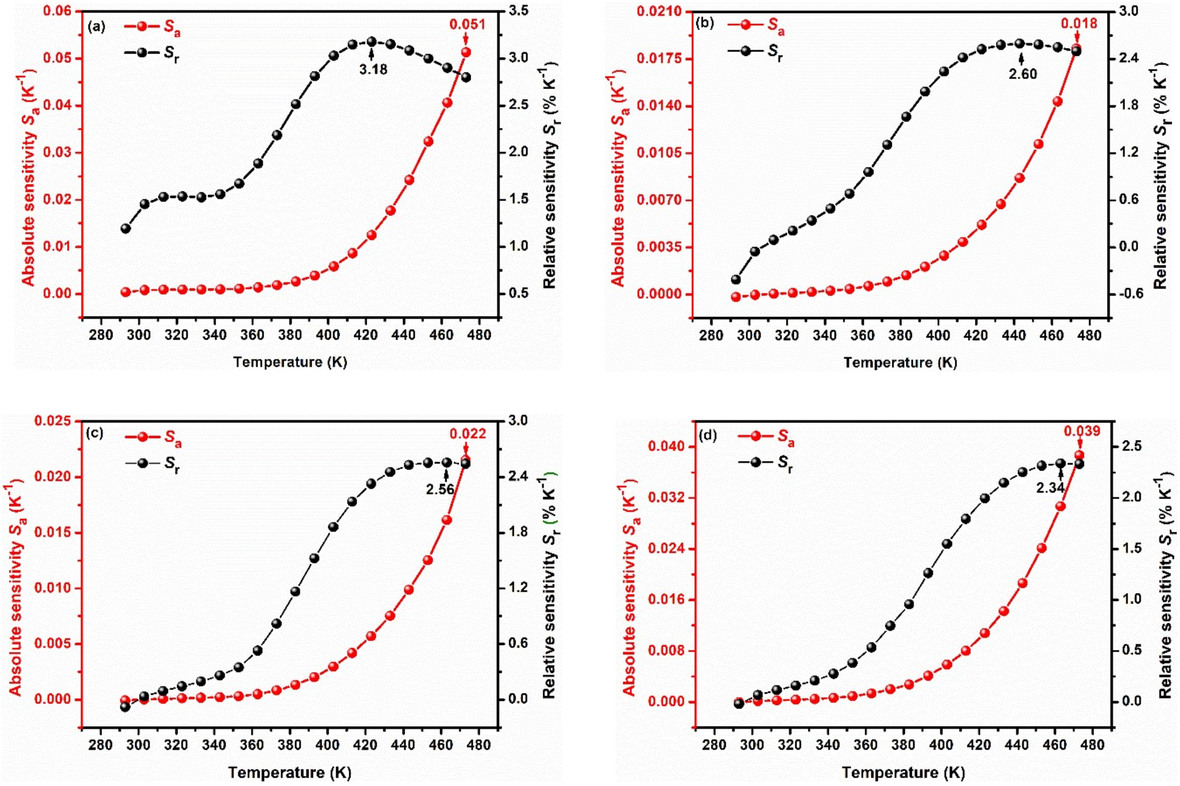

Figure S11 The absolute sensitivity S_a and relative sensitivity S_r of $Li_4SrCaSi_2O_{8-2y}N_{4y/3}$: $0.05Eu^{2+}$ phosphors, (a) y=0, (b) y=0.5, (c) y=1 and (d) y=1.5.

Table S3 Optical thermometry parameters in $Li_4SrCaSi_2O_{8-2y}N_{4y/3}$: $0.05Eu^{2+}$ phosphors

	ΔE_0 (eV)	Maximum S_a (K^{-1})	T_{max} (K)	Maximum S_r (% K^{-1})	T_{max} (K)
y=0	0.554	0.051	473	3.18	423
y=0.5	0.518	0.018	473	2.60	443
y=1	0.544	0.022	473	2.56	463
y=1.5	0.519	0.039	473	2.34	463
y=2	0.535	0.086	473	1.76	473