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Electronic Supplementary Information (ESI)

A rate equation model for the energy transfer mechanism of a novel multi-color-emissive phosphor, $Ca_{1.624}Sr_{0.376}Si_5O_3N_6:Eu^{2+}$

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Table S1 Atomic positions, atomic displacement parameter (U), and site occupancy factor (SOF) obtained after Rietveld refinement using synchrotron powder XRD data of $Ca_{1.624}Sr_{0.376}Si_5O_3N_6$

Atom	Wyckoff site	x/a	y/b	z/c	U ($Å^2$)	SOF
Sr1	2a	0.00000	0.00000	0.00000	0.0165 (8)	0.81
Sr2	2a	0.00000	0.00000	0.50000	0.0170 (8)	0.694
Ca1	2a	0.00000	0.00000	0.00000	0.0165 (8)	0.19
Ca2	2a	0.00000	0.00000	0.50000	0.0170 (8)	0.306
Ca3	4b	0.0155 (10)	0.24770	0.5367 (5)	0.0106 (12)	0.65
Ca4	4b	0.1713 (9)	0.2739 (2)	0.2005 (7)	0.0052 (16)	0.60
Ca5	4b	0.3591 (10)	0.2282 (2)	0.8729 (6)	0.0161 (15)	0.66
Ca6	4b	0.3493 (15)	0.2277 (4)	0.4001 (10)	0.009 (3)	0.35
Ca7	4b	0.1627 (12)	0.2745 (3)	0.7241 (9)	0.002 (2)	0.40
Ca8	4b	0.9880 (13)	0.2477 (4)	0.0652 (9)	0.007 (3)	0.34
Si1	4b	0.1361 (9)	0.4371 (2)	0.6837 (6)	0.0100 (14)	1.0
Si2	4b	0.2720 (8)	0.3697 (2)	0.9805 (5)	0.0143 (14)	1.0
Si3	4b	0.2526 (9)	0.1290 (2)	0.0876 (5)	0.0065 (14)	1.0
Si4	4b	0.2417 (9)	0.1288 (2)	0.5797 (6)	0.0076 (15)	1.0
Si5	4b	0.2620 (8)	0.3697 (2)	0.4502 (5)	0.0063 (14)	1.0
Si6	4b	0.1307 (9)	0.4364 (2)	0.1770 (7)	0.0116 (14)	1.0
Si7	4b	0.3840 (11)	0.0645 (2)	0.8672 (7)	0.0221 (18)	1.0
Si8	4b	0.0032 (12)	0.1388 (3)	0.2685 (7)	0.0183 (16)	1.0
Si9	4b	0.0038 (9)	0.1392 (2)	0.7759 (5)	0.0020 (13)	1.0
Si10	4b	0.3748 (9)	0.06364	0.3698 (6)	0.0001 (11)	1.0
N1	2a	0.785 (3)	0.00000	0.2620 (19)	0.075 (9)	1.0
N2	2a	0.2911 (19)	0.00000	0.8899 (13)	0.019 (3)	1.0
N3	4b	0.1103 (17)	0.4211 (5)	0.4969 (12)	0.010 (3)	1.0
N4	2a	0.238 (2)	0.00000	0.3673 (16)	0.020 (5)	1.0
N5	4b	0.4145 (17)	0.0761 (5)	0.2177 (12)	0.011 (4)	1.0
N6	4b	0.3818 (15)	0.0781 (4)	0.6934 (11)	0.012 (3)	1.0
N7	4b	0.2995 (17)	0.3849 (5)	0.3068 (12)	0.003 (4)	1.0
N8	4b	0.2793 (17)	0.3850 (5)	0.7891 (12)	0.004 (3)	1.0
N9	4b	0.114 (2)	0.4243 (5)	0.0118 (15)	0.009 (4)	1.0
N10	4b	0.2271 (13)	0.1138 (4)	0.4012 (10)	0.022 (2)	1.0
N11	2a	0.7102 (17)	0.00000	0.7416 (11)	0.027 (2)	1.0
N12	4b	0.013 (2)	0.1234 (5)	0.1043 (12)	0.004 (4)	1.0
N13	4b	-0.003 (2)	0.1247 (6)	0.6004 (13)	0.012 (4)	1.0
N14	4b	0.2057 (18)	0.1203 (6)	0.9217 (14)	0.024 (4)	1.0
O1	4b	0.1850 (14)	0.3035 (4)	0.9881 (10)	0.008 (3)	1.0
O2	4b	0.0059 (11)	0.2068 (3)	0.3054 (8)	0.0211 (17)	1.0
O3	4b	0.1837 (16)	0.3053 (5)	0.4580 (11)	0.016 (3)	1.0
O4	4b	0.989 (2)	0.2144 (4)	0.7772 (12)	0.038 (4)	1.0
O5	4b	0.3063 (17)	0.1990 (5)	0.1257 (11)	0.015 (3)	1.0
O6	4b	0.3219 (17)	0.1911 (4)	0.6222 (11)	0.011 (3)	1.0

Compound Name: $Ca_{1.624}Sr_{0.376}Si_5O_3N_6$

Wavelength (λ): 1.5226Å

Space group: *Cm*

Space group No.: 8

No. formula units per unit cell (Z): 8

Lattice parameters: a =7.06115(2) Å, b = 23.78568(5)Å, c = 9.63830(2) Å, β = 109.0841 (2)°.

Table S2 Calculated VASP energy of all the reactants adopted for the formation energy calculation.

	Space Group	**GGA(KJ/mol)**	**HSE06(KJ/mol)**
Sr	*P63/mmc*	-156.846	-151.729
	Fm-3m	-158.381	-153.574
	Im-3m	-156.883	-151.209
Ca	*Fm-3m*	-184.979	-171.396
	Im-3m	-183.343	-169.326
Si	$P6_3/mmc$	-464.23	-528.007
	Ia-3	-507.635	-589.939
	F*d*-3*m*	-523.381	-606.887
O	*C2/m*	-465.704	-611.885
	C2/m	-474.683	-631.278
	R-3*m*	-462.429	-608.498
	Fmmm	-462.059	-609.922
N	$P4_2/mnm$	-802.161	-987.644
	$I2_13$	-655.498	-847.788
	Pa-3	-803.002	-987.901

We adopted the most frequent entry in the ICSD for each binary reactant compound and used their VASP energy for the formation energy calculation. The adopted entries are marked in blue.

Table S3 Initial condition for the Runge-Kutta method (numbers in parenthesis are relative fractions)

Eu concentration	2 mol%	5 mol%	10 mol%
$X_{Eu_g^{2+}(Ca)}$	$8.283 \times 10^{19}/cm^3$ (0.396)	$9.988 \times 10^{19}/cm^3$ (0.191)	$2.081 \times 10^{20}/cm^3$ (0.199)
$X_{Eu_g^{2+}(Sr)}$	$4.790 \times 10^{19}/cm^3$ (0.229)	$1.009 \times 10^{20}/cm^3$ (0.193)	$1.175 \times 10^{20}/cm^3$ (0.164)
$X_{Eu_g^{3+}(Ca)}$	$4.853 \times 10^{19}/cm^3$ (0.232)	$1.522 \times 10^{20}/cm^3$ (0.291)	$3.200 \times 10^{20}/cm^3$ (0.306)
$X_{Eu_g^{3+}(Sr)}$	$2.970 \times 10^{19}/cm^3$ (0.142)	$1.705 \times 10^{20}/cm^3$ (0.326)	$3.462 \times 10^{20}/cm^3$ (0.331)
$X_{Eu_e^{2+}(Ca)}$	0	0	0
$X_{Eu_e^{2+}(Sr)}$	0	0	0
$X_{Eu_e^{3+}(Ca)}$	0	0	0
$X_{Eu_e^{3+}(Sr)}$	0	0	0

The Eu^{3+} content was increased with increasing the total Eu concentration. We used an identical reducing atmosphere for the synthesis of all samples. The reducing atmosphere would not be sufficient for the complete reduction of 10 mol% Eu^{3+}.

1. Radiative rate evaluation

The measured decay time is believed to incorporate information concerning the radiative decay time, non-radiative energy transfer, and temperature-dependent phonon terms for the 5d → 4f emissions of Eu^{2+} in the $Ca_{1.624}Sr_{0.376}Si_5O_3N_6:Eu^{2+}$ host. The measured decay rate, which is the reciprocal of the measured decay time, is the sum of the radiative rate and the other non-radiative rate terms. The non-radiative rate involves both the phonon and energy-transfer rates, as shown by the following relationship:

$$\frac{1}{\tau_{measured}} = \frac{1}{\tau_{radiative}} + \frac{1}{\tau_{phonon}} + \frac{1}{\tau_{ET}} \tag{1}$$

The radiative decay time was not known for $Ca_{1.624}Sr_{0.376}Si_5O_3N_6:Eu^{2+}$, which should be evaluated experimentally for an extremely diluted system at cryogenic temperatures to rule out the non-radiative terms such as energy transfer and phonon. The second term ($1/\tau_{phonon}$) on the right-hand side of Eqn. (1), which comes from the phonon effect, is sensitive to temperature. Direct multi-phonon relaxation would not have significant influence on the Eu^{2+} luminescence, and, therefore the second term on the right-hand side of Eqn. (1) can be ignored. The last term represents the non-radiative energy transfer. If a dipole-dipole interaction was assumed to dominate, the non-radiative energy transfer can be expressed by the following equations.

$$\frac{1}{\tau_{measured}} = \frac{1}{\tau_{radiative}} \left(1 + \left(\frac{R_C}{R}\right)^6\right) + \frac{1}{\tau_{phonon}}$$

$$\frac{1}{\tau_{ET}} = \left(\frac{R_C}{R}\right)^6 \frac{1}{\tau_{radiative}}, \quad R_c\ (or\ R) = \left(\frac{6V}{\pi N x_c\ (or\ x)}\right)^{1/3} \tag{2}$$

Where V is the unit cell volume of the $BaLi_2Al_2Si_2N_6$ host and N is the number of Ba sites in the $Ca_{1.624}Sr_{0.376}Si_5O_3N_6:Eu^{2+}$ unit cell. By definition, the critical energy transfer distance (R_c) is the distance at which the non-radiative decay rate (the non-radiative energy transfer rate) reaches the radiative decay rate. Most of the reported R_c values have been estimated from conventional concentration quenching data. Namely, R_c values are based on critical concentration (x_c), which is indicative of a Eu^{2+} activator concentration with the highest PL intensity in the plot of PL intensity vs. activator concentration.

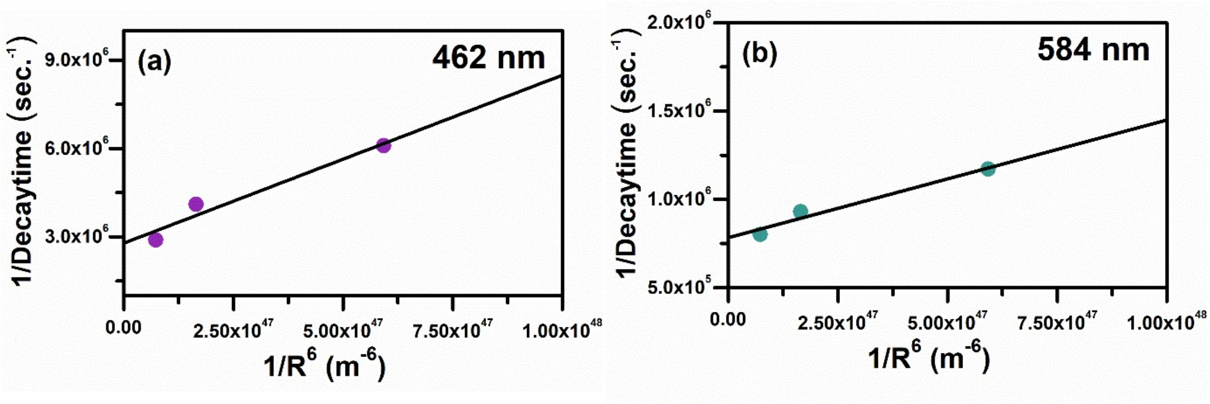

Fig. S1 The plot of $1/\tau_{measured}$ vs. 1/R and its linear regression fit, wherein the 1/R was calculated based on the true Eu^{2+} concentration after the XPS estimation, (a) for 462 nm and (b) for 584 nm emissions.

We elicited an R_c value from the decay curve rather than from the concentration quenching data by strictly obeying the definition of R_c. The true Eu^{2+} concentration was crucial in evaluating legitimate R_c values. An R_c evaluation from the starting Eu_2O_3 concentration would not be appropriate, but a post-analysis of the composition is necessary for a precise estimation of the concentration of Eu^{2+} activators because the valence sate of Eu ions is difficult to control during the synthesis process. The XPS result led to a real Eu^{2+} concentration (x_c).

We also focused on an estimation of the radiative decay time from the measured decay curves together with the exact R_c value for $Ca_{1.624}Sr_{0.376}Si_5O_3N_6:Eu^{2+}$. Fig. S1 (b) shows a plot of $1/\tau_{measured}$ vs. 1/R and its linear regression fit according to Eqn. (2). In this case, the 1/R was converted from the real Eu^{2+} activator concentration obtained from the XPS measurement. The resultant best-fitted parameters such as the radiative decay rate ($1/\tau_{radiative}$) and the critical energy transfer distance (R_c) values were evaluated. The R_c value calculated from the XPS estimation of the Eu^{2+} concentration was 112.7 Å for 460 nm emission and 97.3 Å for 585 nm emission. The radiative rate from the intersect on the vertical axis in Fig. S1(a) and (b) was calculated to be 2.91×10^6 sec^{-1} for 460 nm emission and 7.98×10^5 sec^{-1} for 460 nm emission.

2. Energy transfer theory and Geometry Factor computation details

The exact relationship between the energy transfer constant (kxy) and the energy transfer probability (W_{ET}) is simply expressed as follows:

$$W_{ET} = k_{xy} X_A \ (X_A = acceptor\ concentration)$$

The energy transfer probability was derived as follows:

$$W_{ET} = \frac{3\,e^2\,c^3\,\hbar^5\,\pi}{2\,m}\frac{f_A}{\tau_D}\frac{\int g_A(E)\,g_D(E)\,dE}{E^4}R^{-6} = \frac{1}{\tau_D}\left(\frac{R_C}{R}\right)^6$$ for the dipole-dipole interaction.

The integral term stands for the spectral overlap (SO) between the donor emission and the acceptor absorption, f_A is the oscillator strength for the acceptor absorption, $1/\tau_D$ is the radiative rate for the donor emission, R_C the critical energy transfer radius, and the other symbols denote conventional physics constants. The R^{-6} term can be interpreted as the product of a geometry factor (**Ω**$_{x\text{-}y}$) and the acceptor concentration for a given donor system.

$R^{-6} = \sum \frac{1}{R_i^6} X_A$ (R_i is every possible inter-atomic path within 15 Å around the donor for a certain host structure). The geometry factor (**Ω**$_{x\text{-}y}$) is given as $\sum \frac{1}{R_i^6}$. Consequently, we obtained the following final conclusion;

$$k_{xy} \approx \frac{f_A}{\tau_D} \times SO \times \Omega_{x-y}$$

More details on the geometry factor computation is well described as follows:

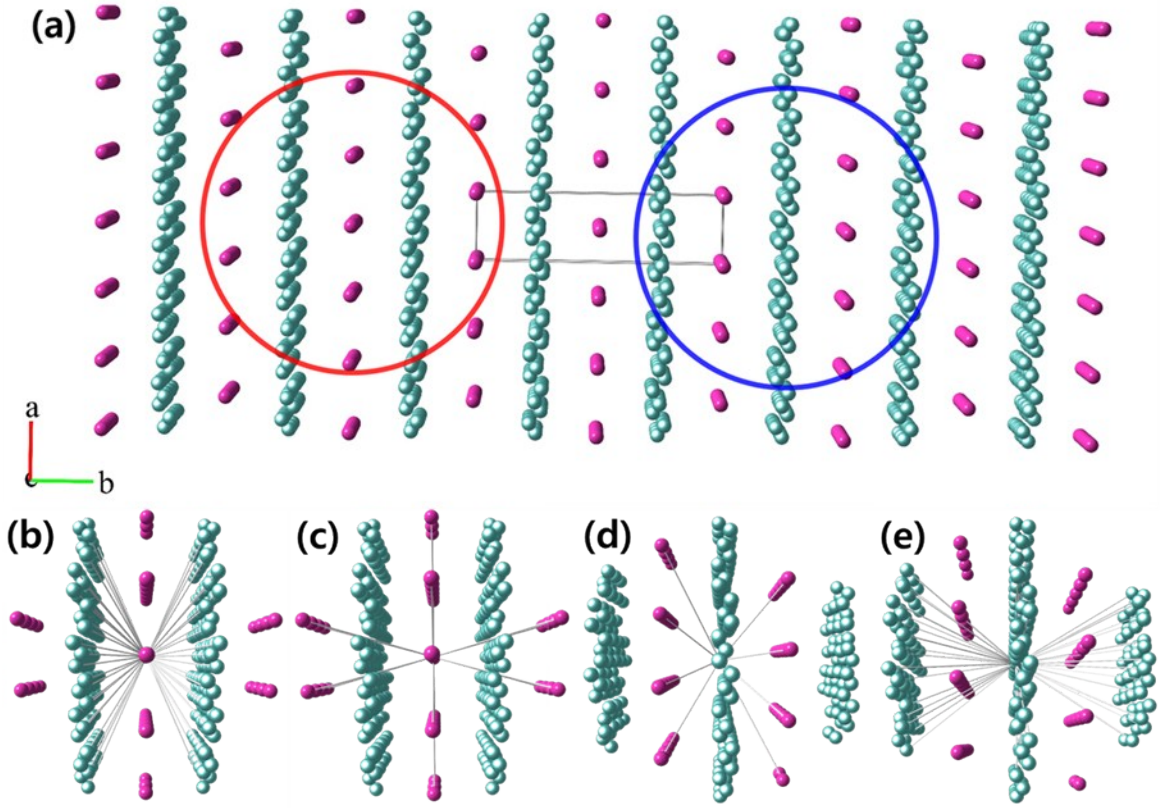

Fig. S2 (a) The $Ca_{1.624}Sr_{0.376}Si_5O_3N_6$ host structure consisting of cations only, representing (b) $\Omega_{Sr\text{-}Ca}$, (c) $\Omega_{Sr\text{-}Sr}$, (d) $\Omega_{Ca\text{-}Sr}$ and (e) $\Omega_{Ca\text{-}Ca}$ for three energy transfer routes in the host.

Fig. S2 shows a schematic explanation for the possible energy transfer routes within 15 Å, which initiated from the highest emission energy site (donor site, the Sr^{2+} site occupied by Eu^{2+} activators) to any other sites that played a luminescent or quenching role. The distance limits of the energy transfer routes were generally restricted within approximately 15 Å. Although this value is smaller than those evaluated in the present study based on real Eu^{2+} concentrations, it would never be problematic since $\frac{1}{R_i^6}$ values beyond 15 Å are negligibly small so that they could never affect the final GF value.

According to the Vasquez analysis model involving various discrete energy transfer routes in the crystalline host [1~5], we calculated a geometry factor excluding any other considerations such as spectral overlap and donor and acceptor concentrations. A dramatic change in the geometry factor with respect to different energy transfer routes showed that this geometrical factor dominantly affected the total energy transfer rate.

$\Omega_{\text{Sr-Ca}} = 6.73 \times 10^{-3}$, $\Omega_{\text{Sr-Sr}} = 5.12 \times 10^{-3}$, $\Omega_{\text{Ca-Sr}} = 1.12 \times 10^{-3}$, $\Omega_{\text{Ca-Ca}} = 1$

References

1. S. O. Vásquez, J. Chem. Phys. 108, 723 (1998).

2. S. O. Vásquez, J. Chem. Phys. 104, 7652 (1996).

3. S. O. Vásquez, J. Chem. Phys. 106, 8664 (1997).

4. S. O. Vásquez, Phys. Rev. B 60, 8575 (1999).

5. S. O. Vásquez, Phys. Rev. B 64, 125103 (2001).