Supporting Information

Narrow-band red phosphors of high colour purity based on Eu^{3+}-activated apatite-type $Gd_{9.33}(SiO_4)_6O_2$

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Table S1. Summary of $^5D_0 \rightarrow {}^7F_J$ transitions observed in luminescence spectra of Eu^{3+}-doped phosphors.

Transition	Dipole character	Range (nm)	Characteristic
$^5D_0 \rightarrow {}^7F_0$	ED	570–585	Only observed for C_n, C_{nv} and C_s site symmetries
$^5D_0 \rightarrow {}^7F_1$	MD	585–600	Independent of environment
$^5D_0 \rightarrow {}^7F_2$	ED	610–630	Strongly dependent on environment
$^5D_0 \rightarrow {}^7F_3$	ED	640–660	Forbidden transition
$^5D_0 \rightarrow {}^7F_4$	ED	680–710	Intensity dependent on environment
$^5D_0 \rightarrow {}^7F_5$	ED	740–770	Forbidden transition
$^5D_0 \rightarrow {}^7F_6$	ED	810–840	Rarely measured and observed

Table S2. Stark sublevels according to the site symmetry of the Eu^{3+} doping site. [8]

Site symmetry	Integer J						
	0	1	2	3	4	5	6
T, T_d, T_h, O, O_h	1	1	2	3	4	4	6
C_{3h}, D_{3h}, C_6, C_{6h}, C_{6v}, D_6, D_{6h}	1	2	3	5	6	7	9
C_3, S_6, C_{3v}, D_3, D_{3d}	1	2	3	5	6	7	9
C_4, S_4, C_{4h}, C_{4v}, D_4, D_{2d}, D_{4h}	1	3	4	5	7	8	10
C_1, C_s, C_2, C_{2h}, C_{2v}, D_2, D_{2h}	1	3	5	7	9	11	13

Table S3. Unit cell parameters for $Gd_{9.33-x}Eu_x(SiO_4)_6O_2$ phosphors.

x	a (Å)	c (Å)	V (Å^3)	R_{wp} (%)	Gd_2SiO_5 (%)
0.03	9.44114(8)	6.869868(8)	530.31(1)	2.28	2.7(8)
0.05	9.4392(1)	6.8699(1)	530.09(2)	2.84	2.6(9)
0.07	9.44102(8)	6.86960(8)	530.27(1)	2.45	2(1)
0.09	9.4399(1)	6.8710(1)	530.26(2)	2.71	4.2(6)
0.19	9.4403(2)	6.8715(2)	530.34(2)	2.93	3.5(8)
0.28	9.4404(1)	6.8703(1)	530.25(2)	3.12	6.3(8)

0.47	9.4444(1)	6.8709(1)	530.76(2)	2.94	0.2(4)
0.65	9.4432(1)	6.8714(1)	530.65(2)	2.99	8(1)
0.93	9.4440(1)	6.8714(1)	530.75(2)	3.52	3.9(9)
1.4	9.4451(2)	6.8760(2)	531.23(3)	3.8	8(1)
1.87	9.4464(1)	6.8778(1)	531.51(2)	3.07	8.0(8)

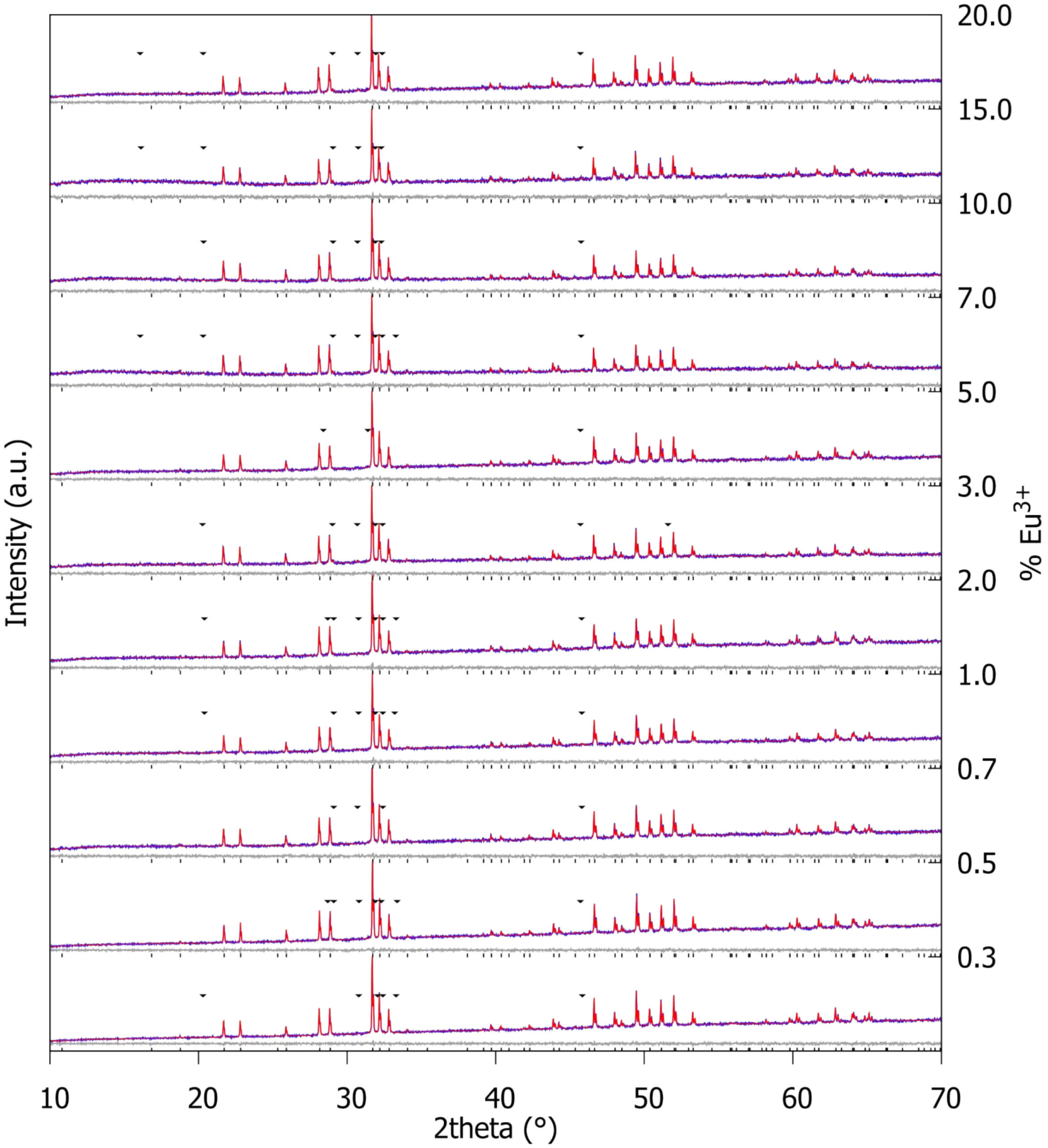

Figure S1. Rietveld fit of the laboratory PXRD data. $Gd_{9.33-x}Eu_x(SiO_4)_6O_2$ (x = 0.03, 0.05, 0.07, 0.09, 0.19, 0.28, 0.47, 0.65, 0.93, 1.40 and 1.87). ∇ indicates the Gd_2SiO_5 impurity peaks.

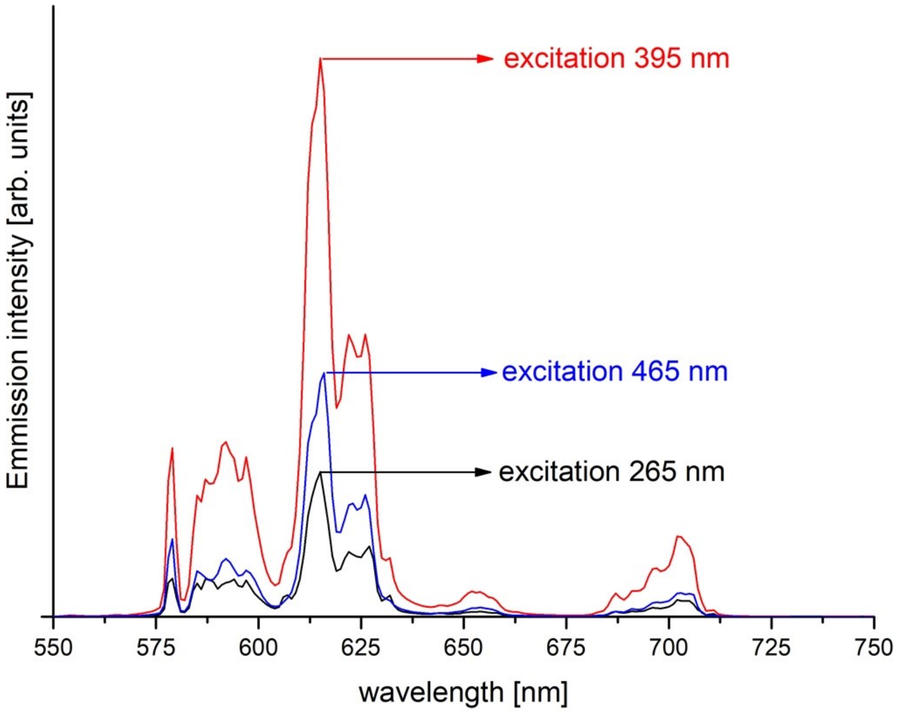

Figure S2. Room-temperature emission spectra of $Gd_{9.05}Eu_{0.28}(SiO_4)_6O_2$ recorded after excitation into the CT band at 265, 396 and 465 nm.

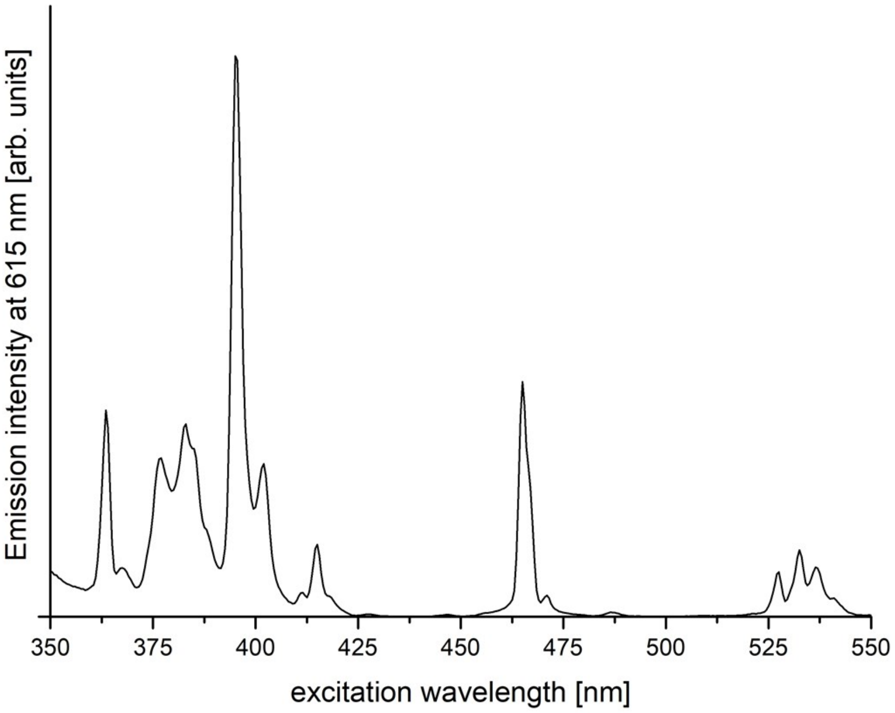

Figure S3. Room-temperature PL excitation spectrum of $Gd_{9.05}Eu_{0.28}(SiO_4)_6O_2$ recorded in the near UV and blue spectral region.

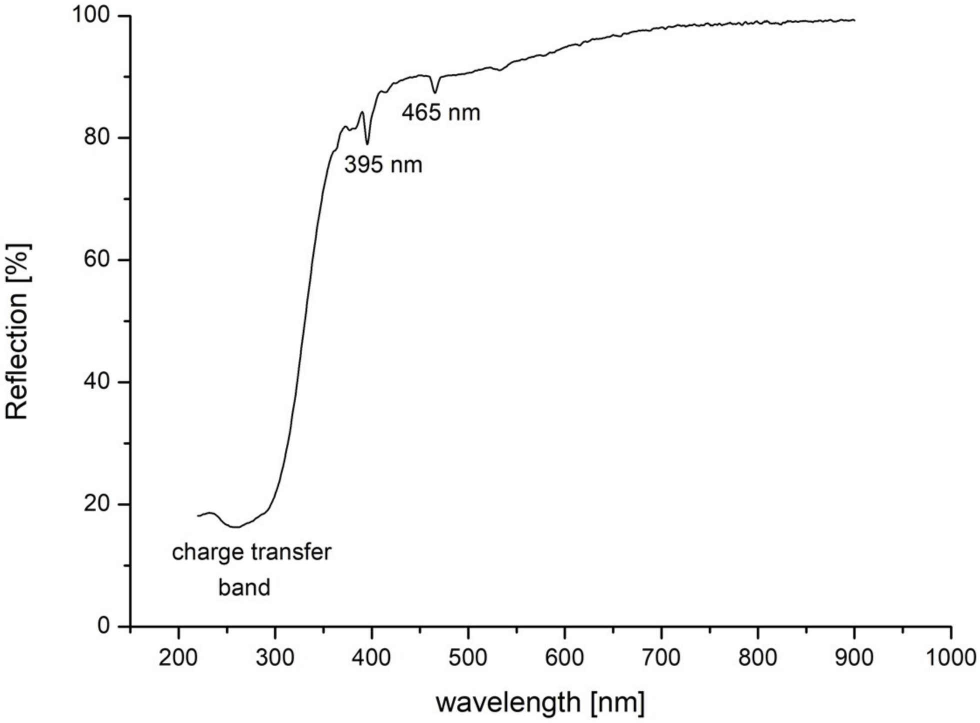

Figure S4. UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) spectra of $Gd_{9.33}(SiO_4)_6O_2$ phosphor host.

Table S4. Thermal expansion coefficients for $Gd_{9.05}Eu_{0.28}(SiO_4)_6O_2$ phosphors.

		T_0 (°C)	T_f (°C)	L_0 (Å)	L_f (Å)
α_a (C^{-1})	8.97(9)E-06	30	500	9.4402(1)	9.4800(1)
α_c (C^{-1})	5.9(1)E-06	30	500	6.8695(1)	6.8886(1)
α_V (C^{-1})	2.4(2)E-05	30	500	530.17(2)	536.14(2)

S1. Judd-Ofelt analysis

The Eu^{3+} ion ($^4f_6$ electron shell) has a very special characteristic: its magnetic dipole (MD) $^5D_0 \rightarrow {}^7F_1$ transition that has a dipole strength which is independent of the environment. Therefore, the dipole strength (D_{MD}) can be calculated and used as a reference for transitions originating from the $^5D_0$ level [6, 11]:

$$D_{MD} = 9.6 \times 10^{-42} esu^2 cm^2 = 9.6 \times 10^{-6} Debye^2, \qquad (1)$$

where 1 esu = $N^{-5/2}$ cm.

The elements of the reduced matrix (U^λ) for electric dipole (ED) transitions originating from $^5D_0$ are zero, with the exception of levels $^7F_\lambda$ (λ = 2, 4, 6), where $U^2 = 0.0032$, $U^4 = 0.0023$ and $U^6 = 0.0002$. [12] The Judd-Ofelt parameters (Equation 2 can be calculated from the ratio of the integrated emission intensity arising from the $^5D_0 \rightarrow {}^7F_\lambda$ (λ = 2, 4, 6) and the MD $^5D_0 \rightarrow\rightarrow {}^7F_1$ transitions. [12]

$$\Omega_\lambda = \frac{D_{MD}\tilde{\nu}_1^3 \quad 9n_1^3 \quad J_\lambda}{e^2\tilde{\nu}_\lambda^3 U^\lambda n_\lambda\left(n_\lambda^2+2\right)^2 J_1}, \tag{2}$$

where Ω_λ are the Judd-Ofelt parameters, n is the refractive index, J_λ is the integrated intensity of the $^5D_0 \rightarrow {}^7F_\lambda$ transition and $\tilde{\nu}_\lambda$ is the average wavenumber of the transition to the $^7F_\lambda$ level.

The ratio of the radiative transition probabilities A_λ of the $^5D_0 \rightarrow {}^7F_\lambda$ ($\lambda = 2, 4, 6$) transitions to the A_1 of the $^5D_0 \rightarrow {}^7F_1$ can be expressed in terms of the ratio of the area S under the respective emission peak,s as given by: [13]

$$\frac{A_\lambda({}^5D_0 \rightarrow {}^7F_\lambda)}{A_1({}^5D_0 \rightarrow {}^7F_1)} = \frac{S({}^5D_0 \rightarrow {}^7F_\lambda)}{S({}^5D_0 \rightarrow {}^7F_1)}, \tag{3}$$

where

$$A_1 = \frac{64\pi^4\tilde{\nu}_1^3}{3h} n_1^3 D_{MD}, \tag{4}$$

$$A_\lambda = \frac{64\pi^4\tilde{\nu}_\lambda^3 n_\lambda \left(n_\lambda^2+2\right)^2}{3h \qquad 9} D_{ED}^\lambda \tag{5}$$

and h is the Planck constant (6.63×10^{-32} N cm).

The theoretical lifetime is obtained from the emission spectrum. The theoretical equation though an approximation, allows the radiative decay to be calculated by means of the emission spectrum, as in Equation 7 [14]:

$$\tau_{theo} = \frac{n_1^{-3} J_1}{14.65 J_T}, \tag{7}$$

where J_T is the total integrated intensity of the emission spectra. The branching ratios (Equation 8) can be used to predict the relative intensity of an emission originating from the $^5D_0$ level.

$$\beta_\lambda = \frac{J_\lambda}{J_T} \tag{8}$$

The intrinsic quantum yield, η, is the ratio of the number of photons emitted to the number of photons absorbed. This can be calculated from the direct observed lifetime and the lifetime calculated from the emission spectrum using Equation 9:

$$\eta = \frac{\tau_{obs}}{\tau_{exp}}. \tag{9}$$

Table S5. Judd-Ofelt parameters, radiative transition possibilities of $^5D_0 \rightarrow {}^7F_\lambda$ ($\lambda = 1, 2, 4$) transitions, radiative theoretical and experimental lifetime values for the $Gd_{9.05}Eu_{0.28}(SiO_4)_6O_2$ phosphors at different temperatures.

Temperature (°C)	Ω_2 (cm^2)	Ω_4 (cm^2)	A_1 (s^{-1})	A_2 (s^{-1})	A_4 (s^{-1})	τ_{rad} (ms)

25	7.28	3.01	84.43	391.71	80.18	1.77
50	7.25	3.03	84.43	389.96	80.75	1.71
75	7.23	3.05	84.44	388.83	81.1	1.71
100	7.11	3.01	84.44	382.3	80	1.79
125	7.15	3.06	84.45	384.22	81.36	1.78
150	7.05	3.05	84.47	378.99	81.27	1.73
175	6.89	3.03	48.48	370.42	80.69	1.76
200	6.68	3.07	84.49	358.77	81.67	1.79
225	6.28	2.98	84.51	337.58	79.31	1.88
250	5.86	3	84.53	315.01	79.92	1.96
275	5.42	3	84.55	291.3	80	2.06
300	5.42	3.02	84.57	270.58	80.74	2.14
325	4.63	3.05	84.59	249.05	81.44	2.24
350	4.32	3.1	84.62	231.94	82.89	2.3
375	4.03	3.16	84.64	216.2	84.7	2.36
400	3.83	3.23	84.65	205.3	86.71	2.39
425	3.68	3.25	84.67	196.77	87.33	2.43
450	3.57	3.23	84.69	190.79	86.67	2.46
475	3.48	3.25	84.7	185.86	87.16	2.47