Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Highly efficient and thermally stable luminescence of $Ca_3Gd_2Si_6O_{18}:Ce^{3+}$, Tb^{3+} phosphors based on efficient energy transfer

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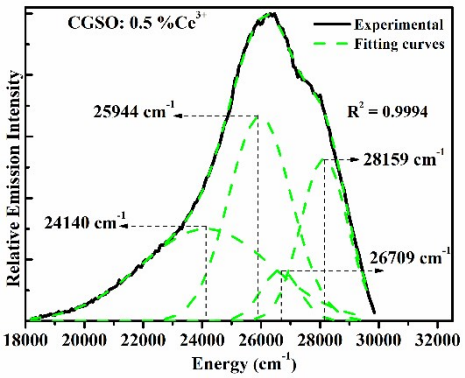

Fig. S1 Gaussian deconvolution of CGSO:0.5%Ce^{3+}.

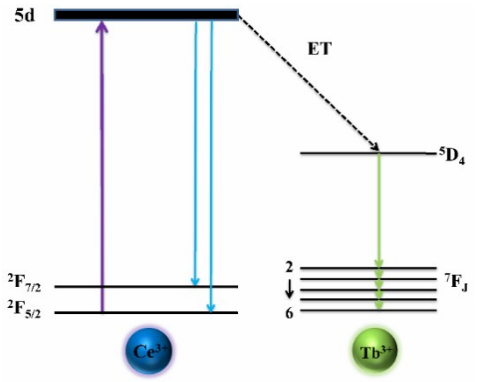

Fig. S2 Energy level diagrams and ET processes of Ce^{3+}→Tb^{3+}.

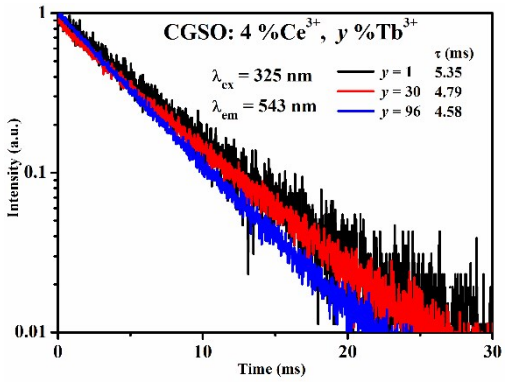

Fig. S3 Fluorescence decay curves of Tb^{3+} in CGSO: 4%Ce^{3+}, *y*%Tb^{3+} (*y* = 0, 30, 96) phosphors (excited at 325 nm, monitored at 543 nm).

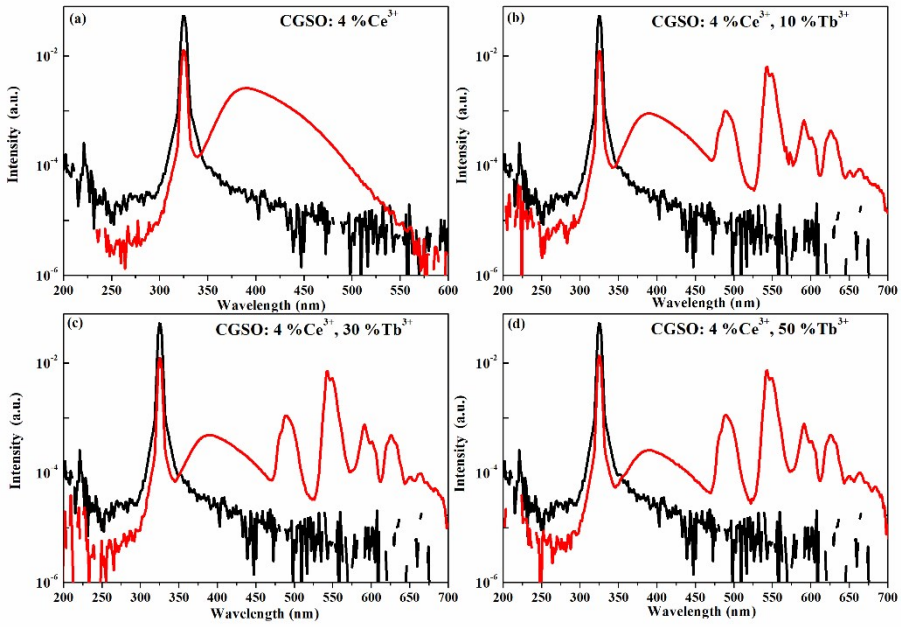

Fig. S4 Emission spectra inside the integrating sphere without (black line) and with (red line) the sample CGSO: 4%Ce^{3+}, *y* Tb^{3+} (*y* = 0, 10, 30, 50) upon 325 nm excitation.

Table S1 The IQE, EQE, the excitation wavelength and the luminescence intensity at 150℃ compared with that at room temperature (LI150) of the selected results from reported references.

samples	IQE (%)	EQE (%)	λ_{ex} nm	LI150 (%)	Refs.
CGSO: 4%Ce^{3+}, 50%Tb^{3+}	90.1	72.4	325	92	This work
$GdBO_3$: 0.02Ce^{3+}, 0.12Tb^{3+}	50.1		361		[1]
$La_3Si_8N_{11}O_4$: 0.01Ce^{3+}, 0.05Tb^{3+}	76.3	46.7	360	90	[2]

$Li_3Sc_2(PO_4)_3$: 0.04Ce^{3+}, 0.005Tb^{3+}	9%		285	47	[3]
$Ba_2Y_{1.74}(SiO_4)_3F$: 2%Ce^{3+}, 40%Tb^{3+}	83.12		355	82	[4]
$CaScAlSiO_6$: 0.02 Ce^{3+}, 0.12Tb^{3+}	79.5		330		[5]
$NaBaScSi_2O_7$: 0.04Ce^{3+}, 0.04Tb^{3+}	36		349	30	[6]
$Ba_2Y_5B_5O_{17}$: 1%Ce^{3+}, 20%Tb^{3+}	76	55	345	92	[7]
$MgY_4Si_3O_{13}$: 0.2Ce^{3+}, 0.4Tb^{3+}	49		330		[8]
$BaY_{1.10}Si_3O_{10}$:0.05Ce^{3+},0.85$Tb^{3+}{}_9$	81.6		337		[9]
Ca_2NaSiO_4F: 0.03Ce^{3+}, 0.15Tb^{3+}	39.3		365	60	[10]
$Lu_5(SiO_4)_3N$: 0.03Ce^{3+}	42.13		359	80	[11]
$Na_3Sc_2(PO_4)_3$: 0.03Ce^{3+}, 0.1Tb^{3+}	65		320	85.6	[12]
$Ca_3Gd(GaO)_3(BO_3)_4$: 0.05Ce^{3+}, 0.3Tb^{3+}	75.5		344		[13]
$Li_2Ca_4Si_4O_{13}$: 0.04Ce^{3+}, 0.08Tb^{3+}	67.3		330		[14]
$Y_5Si_3O_{12}N$: 0.18Ce^{3+}, 0.4Tb^{3+}	85		358	80	[15]
$Sr_3Gd_2(Si_3O_9)_2$: 0.26Ce^{3+}, 0.1Tb^{3+}	80.2		348		[16]
$KSrSc_2(PO_4)_3$: 0.03Ce^{3+}, 0.09Tb^{3+}	66.8		310	88	[17]
$Na_2Ca_3Si_2O_8$： 0.04Ce^{3+}, 0.16Tb^{3+}	85.5		330		[18]
$Ca_3Y_2(Si_3O_9)_2$: 15%Ce^{3+}, 40%Tb^{3+}	77		329		[19]
$Sr_3Y_2(Si_3O_9)_2$: 0.15Ce^{3+}, 0.7Tb^{3+}	90.4		340		[20]
$Ba_2Lu_5B_5O_{17}$: 1%Ce^{3+}, 15%Tb^{3+}	86		348	90	[21]
$Sr_3Lu(PO_4)_3$: 0.04Ce^{3+}, 0.2Tb^{3+}	67.2		310		[22]
$Y_{0.82}Ce_{0.03}Tb_{0.15}BO_3$	76.7		361	87	[23]
$(La_{0.86}Ce_{0.04}Tb_{0.1})PO_4$	84.67		275		[24]
$Ba_3Lu_2B_6O_{15}$:0.03Ce^{3+},0.2Tb^{3+}	51		373	54	[25]
$[Mg_{1.25}Si_{1.25}Al_{2.5}]O_3N_3$:0.03$Ce^{3+}$,0.2$Tb^{3+}$	41.14		335	65	[26]
$Ca_6Ba(PO_4)_4O$: 0.03Ce^{3+},0.01Tb^{3+}	79.6		365	82	[27]
$BaLu_2SiO_3$: 0.06Ce^{3+},0.02Tb^{3+}	71.0		365	97	[28]
$BaGd_2Si_3O_{10}$: 0.04Ce^{3+},0.4Tb^{3+}	62		336	44	[29]
$La_2Si_2O_7$: 0.05Ce^{3+},0.6Tb^{3+}	96		332	89	[30]
$Sr_3Lu_2(BO_3)_4$: 3%Ce^{3+}, 8%Tb^{3+}	77.5	34.8	340	70	[31]
$Ba_3Y_2B_6O_{15}$: 0.03Ce^{3+},0.3Tb^{3+}	49		365	22	[32]
$La_8Ba_2(Si_4P_2O_{22}N_2)O_2$:0.005$Ce^{3+}$,0.1$Tb^{3+}$	89		290	91.2	[33]
$La_{0.59}Al_{2.03}B_4O_{10.54}$: 0.06$Ce^{3+}$, 0.35 Tb^{3+}	40.9		310	56	[34]
$NaBa_4(AlB_4O_9)_2Cl_3$:0.09Ce^{3+}, 0.13Tb^{3+}		43.38	323	95.22	[35]
$Sr_2MgB_2O_6$:0.05 Ce^{3+},0.05 Tb^{3+}	66.39	48.92	323	75.3	[36]
$Ca(Mg_{0.8}Al_{0.2})(Si_{1.8}Al_{0.2})O_6$:0.03$Ce^{3+}$,0.03$Tb^{3+}$	36.81		340	70.5	[37]
$Ca_2YHf_2Al_3O_{12}$: 0.03Ce^{3+},0.6Tb^{3+}	78.5	56	408	43.3	[38]
Al_5O_6N: 0.003Eu^{2+}, 0.01Tb^{3+}	11.1		330	51	[39]
$Sr_3NaSc(PO_4)_3F$: 0.03Eu^{2+}, 0.5Tb^{3+}	9.4		365	67	[40]

Table S2 Rietveld refinement, crystallographic and structure parameters of the representative samples CGSO: 4%Ce^{3+}.

Compound	$x = 0$
Space group	$P6_3/m$

a (Å)	13.4025(1)
b (Å)	7.7878(1)
c (Å)	14.8698(5)
α (deg)	90
β (deg)	90.25
γ (deg)	90
V (Å^3)	1552.049
Z	4
R_p (%)	5.45
R_{wp} (%)	8.02
R_{exp} (%)	3.55
χ^2	5.10

According to Dexter's ET expressions of multipolar interactions and Reisfeld's approximation, the following relation can be obtained [41]:

$$\frac{\eta_0}{\eta} = C^{n/3} \tag{S1}$$

where C is the total doping concentration of Ce^{3+} and Tb^{3+}, η_0 and η are the quantum efficiencies of Ce^{3+} in the absence and presence of Tb^{3+}, n = 6, 8, and 10 corresponding to dipole−dipole, dipole−quadrupole and quadrupole−quadrupole interactions, respectively. The value η_0/η can be approximately estimated by the ratio of related emission intensities as [27]:

$$\frac{I_0}{I} = C^{n/3} \tag{S2}$$

where I_0 and I are the emission intensities of Ce^{3+} in the absence and presence of Tb^{3+}. The plots of I_0/I versus $C^{n/3}$ are presented in Fig. S5. The best linear relationship can be achieved at n = 8, implying that the dipole−quadrupole interaction governs the ET process from Ce^{3+} to Tb^{3+}.

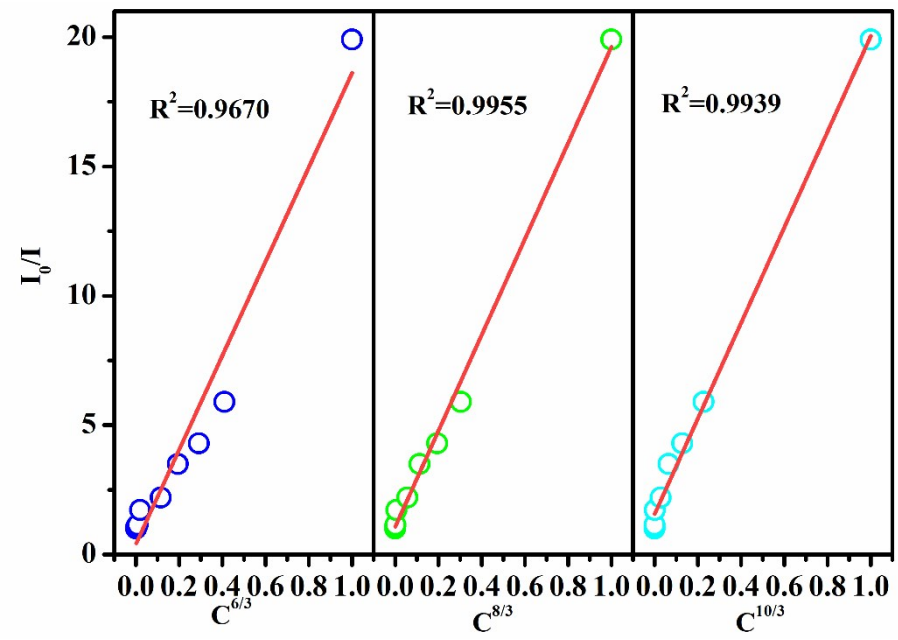

Fig. S5 Dependence of I_0/I of Ce^{3+} on $C^{6/3}$, $C^{8/3}$ and $C^{10/3}$.

The ET efficiency η_{ET} from Ce^{3+} to Tb^{3+} can be calculated based on the effective lifetime by using the following equation:

$$\eta_{ET} = 1 - \frac{\tau}{\tau_0} \quad \text{(S3)}$$

where τ and τ_0 are the lifetimes of Ce^{3+} in the presence and in the absence of Tb^{3+}, respectively. The calculated ET efficiencies from Ce^{3+} to Tb^{3+} using Eq. S1 were given in Table S3.

The energy transfer efficiency from Ce^{3+} to Tb^{3+}, η'_{ET} can be calculated based on the Tb^{3+} concentration dependence of the emission intensity of Ce^{3+} shown in Fig. 4, by using the following Equation:

$$\eta_{ET}^{'} = 1 - \frac{I}{I_0} \quad \text{(S4)}$$

where I_0 and I are the emission intensities of Ce^{3+} in the absence and in the presence of Tb^{3+}, respectively. The calculated ET efficiencies from Ce^{3+} to Tb^{3+} using Eq. S2 were given in Table S3.

Table S3 Calculated energy transfer efficiencies of CGSO: 4%Ce^{3+}, y%Tb^{3+} (x=0-96).

y	η_{ET} =1-I/I_0 (%)	η'_{ET} =1-τ/τ_0 (%)
0	0	0
1	0.07	0.09

5	0.08	0.13
10	0.15	0.41
30	0.32	0.55
40	0.43	0.71
50	0.54	0.77
60	0.57	0.83
96	0.63	0.96

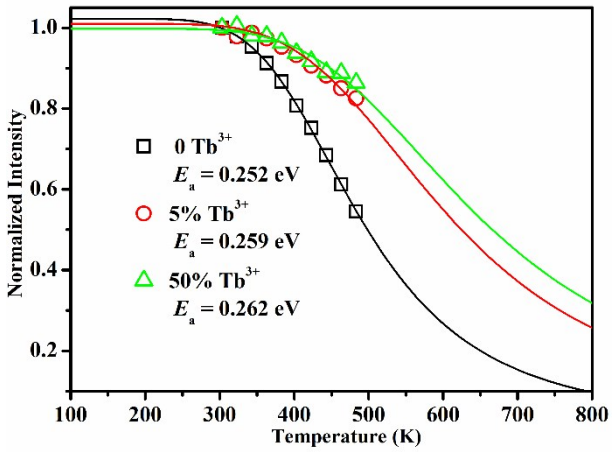

Fig. S6 Plots of normalized total emission intensities versus temperatures for CGSO: 4%Ce^{3+}, y%Tb^{3+} (y = 0, 5, 50).

The activation energy ΔE_a was calculated using the Arrhenius equation given as [42]:

$$I(T) = \frac{I0}{1 + Ae^{\left(-\Delta E_a / k_B T\right)}}$$

where $I0$ is the initial total emission intensity of the phosphor at absolute zero, I(T) is the total emission intensity at a given temperature T, A is a constant, ΔE_a is the activation energy for thermal quenching, and k_B is the Boltzmann constant (8.617×10^{-5} eVK^{-1}). Fig. S6 depicts the plots of normalized total emission intensities versus temperatures for CGSO: 4%Ce^{3+}, y%Tb^{3+} (y = 0, 5, 50). Through the best fit using the Arrhenius equation, ΔE_a were obtained to be 0.252 eV, 0.259 eV, and 0.262 eV for CGSO: 4%Ce^{3+}, y%Tb^{3+} (y = 0, 5, 50), respectively.

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