Electronic Supplementary Material (ESI) for Dalton Transactions.

Energy Transfer and Tunable Emission in $BaSrGd_4O_8:Bi^{3+},Eu^{3+}$ Phosphors for Warm WLED

Shuai Wei, [a, b] *Zeyu Lyu,* [b*] *Dashuai Sun,* [b] *Pengcheng Luo,* [a, b] *Zheng Lu,* [b] *Luhui Zhou,* [b] *Mingrui He,* [b] *Sida Shen,* [b] *Hongpeng You* [a, b, c*]

a Nanchang University, School of Chemistry and Chemical Engineering, Nanchang 330031, P. R. China

b Key Laboratory of Rare Earths, Chinese Academy of Sciences; Ganjiang Innovation Academy, Chinese Academy of Sciences, Ganzhou 341000, P. R. China

c State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

* Corresponding author. Fax: +86 431 85698041. E-mail address: hpyou@ciac.ac.cn (H.P. You), zylyu@gia.cas.cn (Z.Y. Lyu).

Supplementary Notes

Supplementary Notes 1：

The critical distance (R_c) between the nearest Bi^{3+} ions in this phosphor be approximated by the following formula:

$$R_c \approx 2\left[\frac{3V}{4\pi X_c N}\right]^{\frac{1}{3}}$$

Where V is the unit cell volume, X_c refers to the critical concentration of the activating ions, and N stands for the number of total Bi^{3+} sites in the unit cell. As for this phosphor, V = 440.446 $Å^3$, X_c = 0.02, and N = 8, and the value of R_c can be calculated to be 17.39 Å. As for the exchange interaction, the critical distance is about 5 Å, which is much smaller than that of BSGO:Bi^{3+}. Therefore, the energy transfer in BSGO:Bi^{3+} is via the electrical multipole interactions. On the basis of the Dexter theory, the following equation can be used to specify the interaction type:

$$log\left(\frac{I}{x}\right) = -\frac{\theta}{3}logx + A$$

Where x and I represent the activator ion concentration and its corresponding emission intensity, respectively. A is a constant under the same excitation condition. By analyzing the value of the parameter θ in this equation, the energy transfer mechanism of the electric multipole interaction can be approximated. The values of θ = 6, 8 and 10 correspond to the electric dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, respectively. As shown in Figure S2, the slope of the fitted line between log(I/x) and log(x) is 1.44. Hence, the value of θ is 4.32, which

is close to 6, indicating that the concentration quenching mechanism of Bi^{3+}-doped BSGO phosphor is due to the dipole-dipole interaction.

Supplementary Notes 2：

The PL decay curves were fitted using single exponential functions:

$$I = I_0 exp\left(-\frac{t}{\tau}\right)$$

where I represent luminescence intensity, t denotes lifetime, and τ refers to decay time for different components. The PL lifetime τ can be calculated by the following formula:

$$\tau = \frac{\int_{\infty}^{0} tI(t)dt}{\int_{\infty}^{0} I(t)dt}$$

where $I(t)$ is the luminescent intensity at time t. Monitored at 410 nm and 465 nm, for both sites, the decay lifetimes of 277.87 and 320.37 ns.

Supplementary Notes 3：

The absorption efficiency (ξabs), internal quantum efficiency (IQE), and external quantum efficiency (EQE) can be respectively calculated by the following formula:

$$\xi_{abs} = \frac{\int E_R - \int E_s}{\int E_R}$$

$$IQE = \frac{\int L_s}{\int E_R - \int E_s}$$

$$EQE = IQE \times \xi_{abs}$$

where $\int L_s$ represents the integral area of emission spectrum, $\int E_R$ and $\int E_s$ represent the integral area of excitation spectrum without and with the phosphor in the integrating sphere, respectively. As shown in the Figure 2i, under 344 nm excitation, the values of IQE, ξabs and EQE of and BSGO:0.02Bi^{3+},1.0wt% SrF_2 are calculated to be 33.92%, 82.05% and 27.83%, respectively.

Table S1. Refined structural data of BSGO samples.

Samples	Cell parameters (Å)			Volume ($Å^3$)	R_{wp}, R_p, (%), χ^2
	a	b	c		
BSGO	10.3400	3.4995	12.1807	440.754	4.87, 3.87, 0.1726
BSGO:0.02Bi^{3+}	10.3335	3.4993	12.1806	440.446	5.05, 4.01, 0.1886
BSGO:0.02Bi^{3+}, 0.04Eu^{3+}	10.3319	3.4987	12.1770	440.178	5.13, 4.02, 0.1941

Table S2. The atom positions, fraction factors, and thermal vibration parameters of BSGO samples.

Formula		$BaSrGd_4O_8$			
element	occupancy	x	y	z	uiso
Ba1	0.5	0.7514	0.25	0.6488	0.01476
Sr1	0.5	0.7514	0.25	0.6488	0.01476
Gd1	1	0.4209	0.25	0.612	0.01476
Gd2	1	0.4236	0.25	0.1117	0.01476
O1	1	0.214	0.25	0.1707	0.02096
O2	1	0.1215	0.25	0.483	0.02096
O3	1	0.505	0.25	0.786	0.02096
O4	1	0.43	0.25	0.4152	0.02096

Formula		$BaSrGd_4O_8$:$0.02Bi^{3+}$			
element	occupancy	x	y	z	uiso
Ba1	0.5	0.7514	0.25	0.6488	0.01501
Sr1	0.5	0.7514	0.25	0.6488	0.01501
Gd1	0.98	0.4209	0.25	0.612	0.01501
Bi1	0.02	0.4209	0.25	0.612	0.01501
Gd2	0.98	0.4236	0.25	0.1117	0.01501

Bi2	0.02	0.4236	0.25	0.1117	0.01501
O1	1	0.214	0.25	0.1707	0.02122
O2	1	0.1215	0.25	0.483	0.02122
O3	1	0.505	0.25	0.786	0.02122
O4	1	0.43	0.25	0.4152	0.02122

Formula		$BaSrGd_4O_8$:0.02Bi^{3+},0.04Eu^{3+}			
element	occupancy	x	y	z	uiso
Ba1	0.5	0.7514	0.25	0.6488	0.01667
Sr1	0.5	0.7514	0.25	0.6488	0.01667
Gd1	0.94	0.4209	0.25	0.612	0.01667
Bi1	0.02	0.4209	0.25	0.612	0.01667
Eu1	0.04	0.4209	0.25	0.612	0.01667
Gd2	0.94	0.4236	0.25	0.1117	0.01667
Bi2	0.02	0.4236	0.25	0.1117	0.01667
Eu2	0.04	0.4236	0.25	0.1117	0.01667
O1	1	0.214	0.25	0.1707	0.02288
O2	1	0.1215	0.25	0.483	0.02288
O3	1	0.505	0.25	0.786	0.02288
O4	1	0.43	0.25	0.4152	0.02288

WLED	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	R15
1	91.9	99.0	95.5	94.5	93.3	95.0	97.3	98.6	98.4	95.7	95.0	95.4	91.5	95.3	94.3
2	81.3	91.7	81.8	75.7	79.6	81.7	88.1	97.0	97.2	92.6	90.8	90.1	84.3	90.3	88.4

Table S3. The values of R1-R15 for WLEDs.

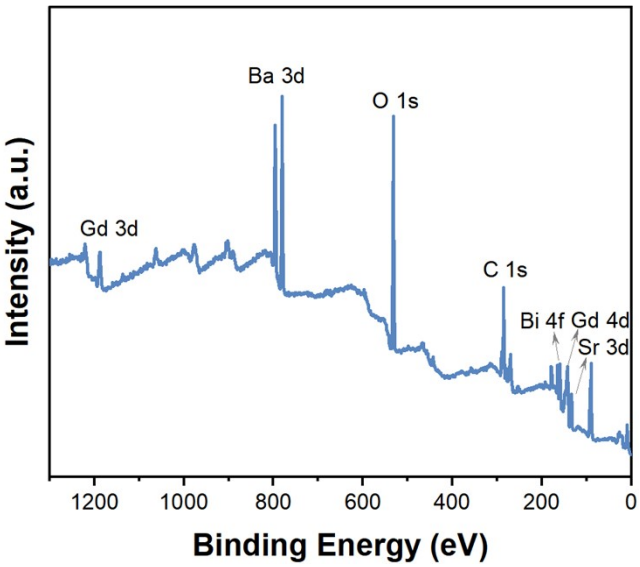

Figure S1. XPS spectra of the BSGO:Bi^{3+} phosphor.

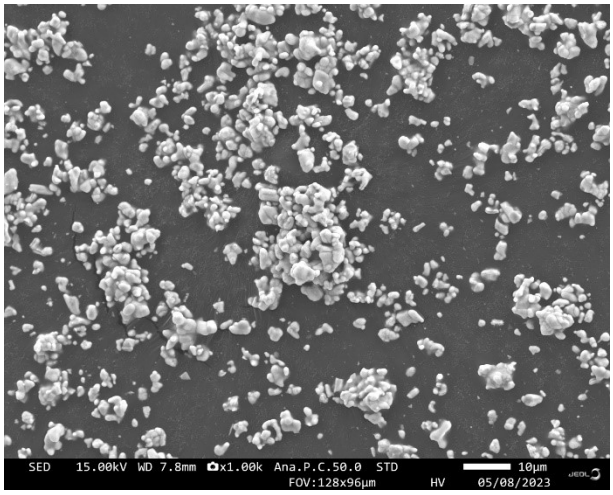

Figure S2. SEM image of BSGO:0.02Bi^{3+},0.04Eu^{3+} phosphor.

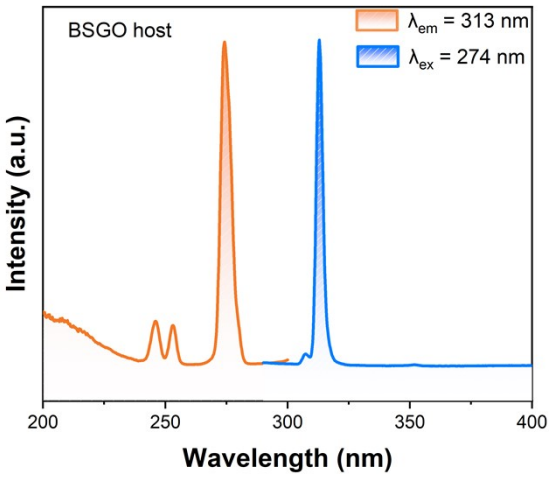

Figure S3. PL-PLE spectra of BSGO host.

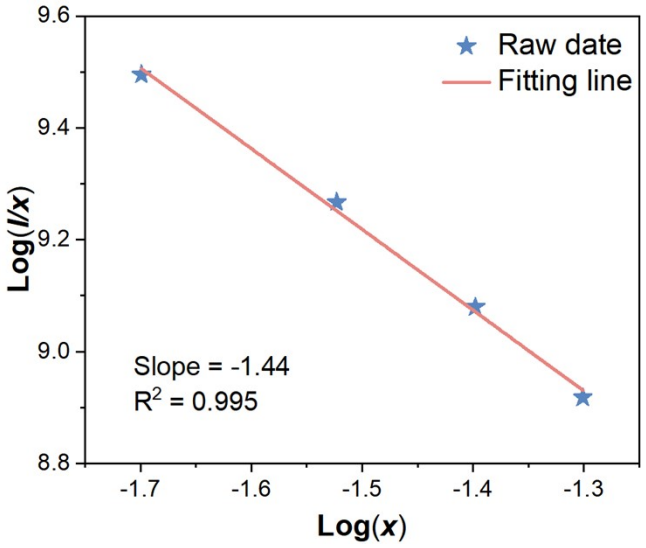

Figure S4. Linear relationship of log(I/x) versus log(x) in BSGO:*x*Bi^{3+}.

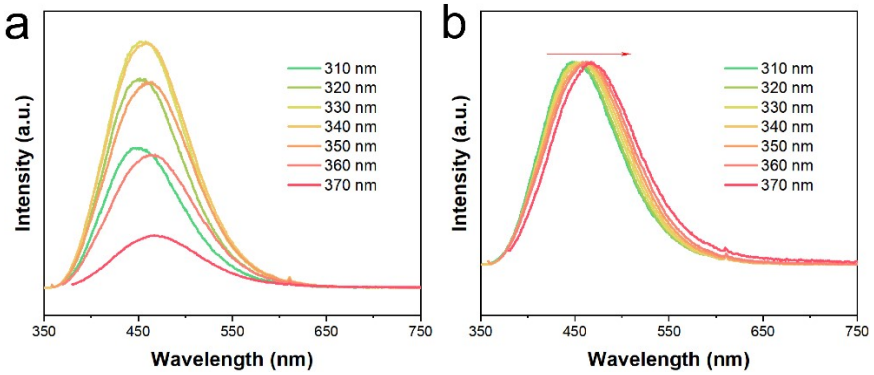

Figure S5. (a) PL emission spectra of BSGO:Bi^{3+} excited at 310 nm – 370 nm. (b) Normalized PL emission spectra of BSGO:Bi^{3+} excited at 310 nm – 370 nm.

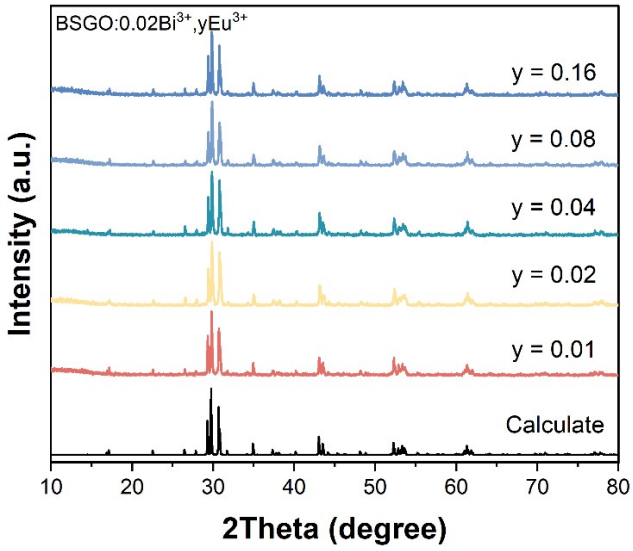

Figure S6. XRD patterns of the BSGO:0.02Bi^{3+},*y*Eu^{3+} (y = 0.01 – 0.16) samples.

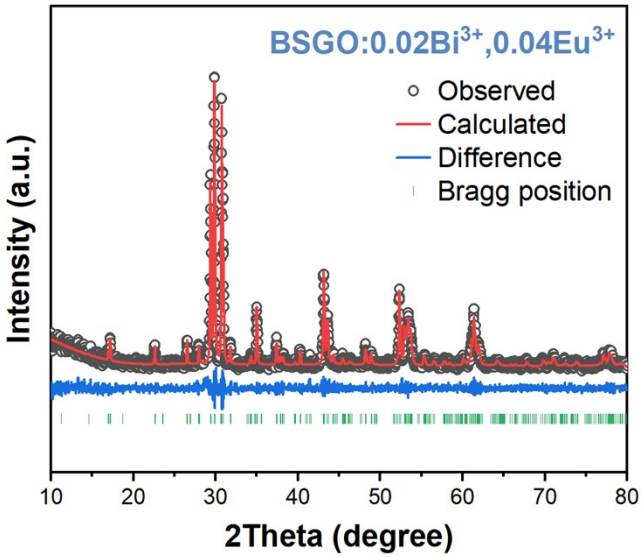

Figure S7. Rietveld refinements for BSGO:0.02Bi^{3+},0.04Eu^{3+}.

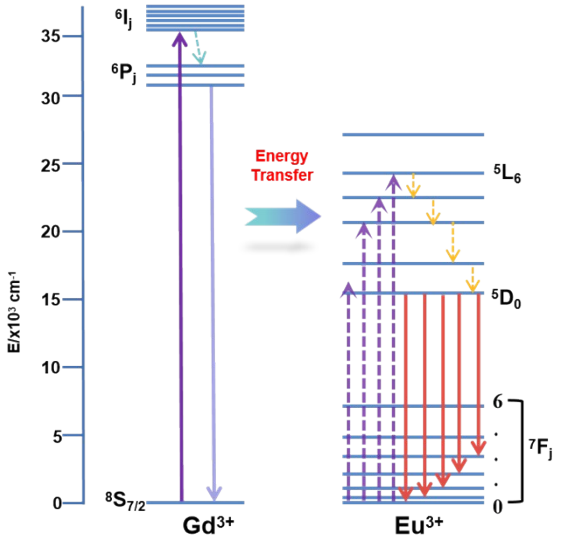

Figure S8. Schematic diagram of the possible energy transfer from Gd^{3+} to Eu^{3+}.

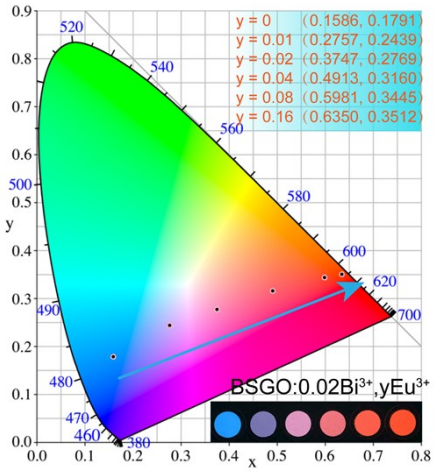

Figure S9. CIE chromaticity coordinates BSGO:0.02Bi^{3+},*y*Eu^{3+} (y = 0 – 0.16) phosphors and inset is a digital photo of the phosphors under the 365nm UV light.