Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

A Multi-centre Activated Single-phase White Light Phosphor with High Efficiency for Near-UV Based WLEDs

Ziwang Zhang, [a] Nan Yang, [a] Zhuo Li, [a] Jun Chen, [a] Pin Chen, [b] Yiqin Xu, [c] Jianxin Shi *[a] and Mingmei Wu *[a,d]

[a] *School of Chemistry, Sun Yat-Sen University, Guangzhou 510006, P. R. China*

[b] *National Supercomputer Center in Guangzhou, School of Computer Science and Engineering, Sun Yat-Sen University, Guangzhou 510006, P. R. China*

[c] *Guangdong Institute of Semiconductor Industrial Technology, Guangzhou 510650, P. R. China.*

[d] *School of Chemical Engineering and Technology, Sun Yat-Sen University, Zhuhai 519082, P. R. China*

* Corresponding authors: cessjx@mail.sysu.edu.cn, ceswmm@mail.sysu.edu.cn

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Remark: The sequence of the table of contents is consistent with the order of the relevant content appearing in the manuscript.

Table S1 The refined atomic parameters of GSBO.

Atom	Wyckoff site	*x*	*y*	*z*	U_{iso}	S.O.F
Gd	8*d*	-0.0175	0.41672	0.8191	0.030	1.00
Sr1	8*d*	-0.1925	0.37501	0.34473	0.030	1.00
Sr2	4*c*	0.1791	1/4	0.5304	0.006	1.00
B1	8*d*	-0.175	0.537	0.511	0.170	1.00
B2	4*c*	-0.514	1/4	0.395	0.037	1.00
B3	4*c*	0.197	1/4	0.819	0.670	1.00
O1	8*d*	-0.1170	0.5908	0.4568	0.142	1.00
O2	8*d*	-0.0961	0.5431	0.6803	0.112	1.00
O3	8*d*	-0.2949	0.4951	0.518	0.089	1.00
O4	4*c*	-0.375	1/4	0.2405	0.087	1.00
O5	8*d*	-0.5585	0.3280	0.4355	0.036	1.00
O6	8*d*	0.2335	0.3169	0.8003	0.068	1.00
O7	4*c*	-0.1389	1/4	0.522	0.053	1.00

Space group: *Pnma* (62)

Cell parameters: a = 7.4195 Å, b = 16.0419 Å, c = 8.7596 Å,
$\alpha = \beta = \gamma = 90°$, V = 1042.60 Å^3, Z = 4

Reliability factors: R_{wp} = 2.95%, R_p = 2.23%

Table S2 The refined atomic parameters of GSBO:0.03Ce^{3+},0.18Tb^{3+},0.05Sm^{3+}.

Atom	Wyckoff site	*x*	*y*	*z*	U_{iso}	S.O.F
Gd	8*d*	-0.0153	0.4168	0.8208	0.018	0.74
Ce	8*d*	-0.0153	0.4168	0.8208	0.018	0.03
Tb	8*d*	-0.0153	0.4168	0.8208	0.018	0.18
Sm	8*d*	-0.0153	0.4168	0.8208	0.018	0.05
Sr1	8*d*	-0.1955	0.3749	0.3455	0.014	1.00
Sr2	4*c*	0.1807	1/4	0.5309	0.012	1.00
B1	8*d*	-0.203	0.561	0.533	0.607	1.00
B2	4*c*	-0.510	1/4	0.375	0.038	1.00
B3	4*c*	0.262	1/4	0.827	0.543	1.00
O1	8*d*	-0.127	0.5818	0.448	0.174	1.00
O2	8*d*	-0.087	0.5493	0.689	0.079	1.00
O3	8*d*	-0.290	0.5027	0.517	0.041	1.00
O4	4*c*	-0.365	1/4	0.250	0.034	1.00
O5	8*d*	-0.555	0.3213	0.437	0.024	1.00
O6	8*d*	0.2399	0.3155	0.8007	0.012	1.00
O7	4*c*	-0.139	1/4	0.509	0.03	1.00

Space group: *Pnma* (62)

Cell parameters: a = 7.4244 Å, b = 16.0184 Å, c = 8.7620 Å,
$\alpha = \beta = \gamma = 90°$, V = 1042.04 Å^3, Z = 4

Reliability factors: R_{wp} = 4.63%, R_p = 3.37%

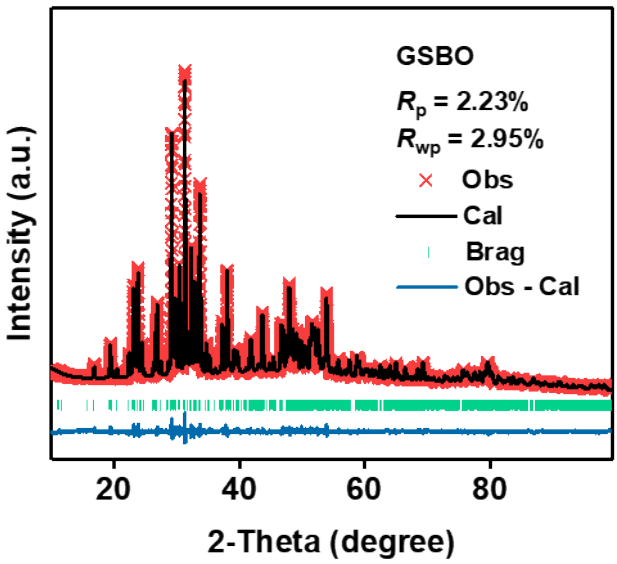

Fig. S1 The Rietveld refinement profile of GSBO.

Table S3 The atomic ratio of GSBO:0.03Ce^{3+},0.18Tb^{3+},0.05Sm^{3+}.

Elements	Atomic (%)	Calculated (%)	Stoichiometric (%)
Sr	20.77	/	/
Gd	9.66	75.76	74.0
Ce	0.38	2.98	3.0
Tb	2.17	17.02	18.0
Sm	0.54	4.24	5.0

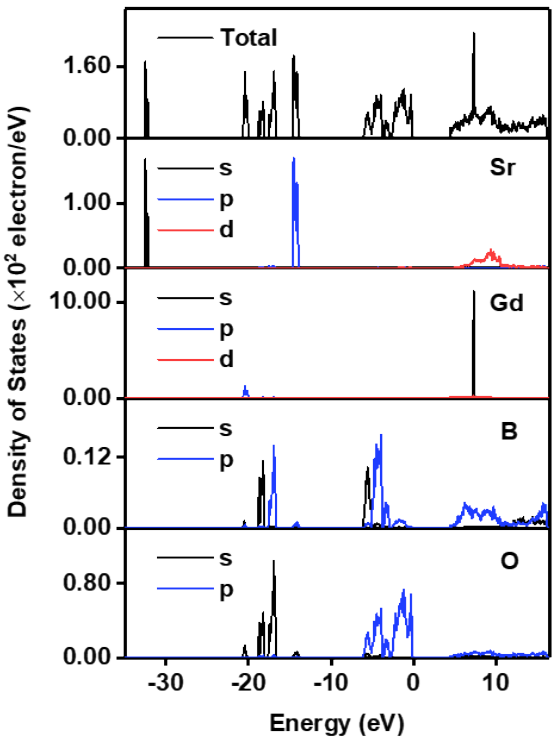

Fig. S2 The total/projected electron density of states of GSBO.

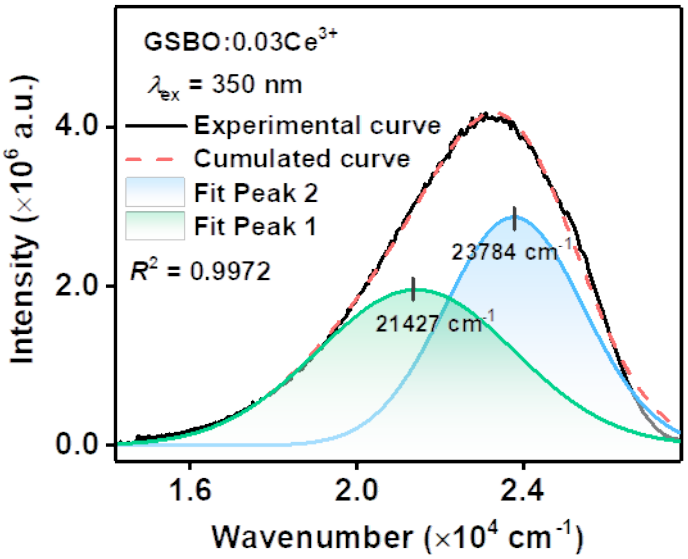

Fig. S3 The Gaussian fitting of the PL spectrum of GSBO:0.03Ce^{3+}.

The Gaussian fitting of the PL spectrum of GSBO:0.03Ce^{3+} is presented in Fig. S3. The emission peak of GSBO:0.03Ce^{3+} can be well fitted with two sub-bands which locate at 21427 cm^{-1} and 23784 cm^{-1}. Since the energy difference of $^2F_{5/2}$ and $^2F_{7/2}$ is about 2000 cm^{-1}, these sub-bands should originate from the 5d excited state to the ground states of Ce^{3+} ($^2F_{5/2}$ and $^2F_{7/2}$).[1]

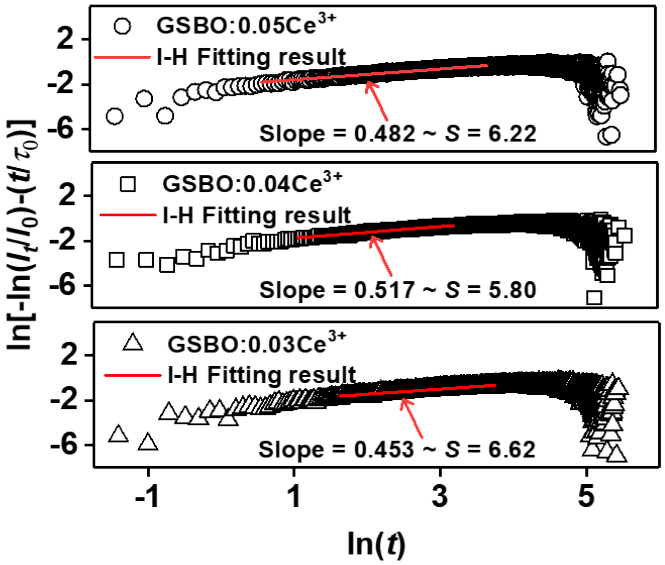

Fig. S4 The I-H fitting of the GSBO:0.03Ce^{3+}, GSBO:0.04Ce^{3+} and GSBO:0.05Ce^{3+}.

Apart from the I-H fitting function mentioned in the manuscript, the value of *S* can also be fitted by following equation: [2,3]

$$\ln\left(-\ln\left(\frac{I_t}{I_0}\right)-\left(\frac{t}{\tau_0}\right)\right)=A+\frac{3}{S}\ln(t)\#(1)$$

where *A* is the control factor, τ_0 is the lifetime of donors without acceptors, here we also chose the lifetime of the least quenched samples (GSBO:0.01Ce^{3+}) as τ_0 to fit the decay curves of GSBO:0.03Ce^{3+}, GSBO:0.04Ce^{3+} and GSBO:0.05Ce^{3+}. All the values of *S* of the three samples are estimated to be about 6, suggesting that D-D interaction should be the dominant energy migration mechanism in Ce^{3+} singly-doped samples.

Table S4 The critical distances between Ce^{3+} - Tb^{3+}, Ce^{3+} - Sm^{3+} and Tb^{3+} -Sm^{3+}.

Doubly-doped samples	V (Å^3)	x_C	N	R_C (Å)
Ce^{3+} - Tb^{3+}	1042.60	0.15	8	11.84
Ce^{3+} - Sm^{3+}	1042.60	0.08	8	14.60
Tb^{3+} - Sm^{3+}	1042.60	0.51	8	7.87

In general, the energy transfer between donor and acceptor should occur *via* exchange interaction or multipolar interaction. In order to identify which mechanism dominates in GSBO host, the critical distances between Ce^{3+} - Tb^{3+}, Ce^{3+} - Sm^{3+} and Tb^{3+} -Sm^{3+} are estimated by the following equation: [4,5]

$$R_c = 2\left(\frac{3V}{4\pi x_C N}\right)^{\frac{1}{3}} \#(2)$$

where V is the volume of the host's unit cell, x_C is the critical concentration and N is the number of cation position that dopants can replace in the unit cell. Here, the values of V, N and x_C of Ce^{3+} - Tb^{3+}, Ce^{3+} - Sm^{3+} and Tb^{3+} - Sm^{3+} co-doped samples are listed in Table S4. Therefore, the values of critical distance for doubly-doped samples can be estimated to be 11.84 Å, 14.60 Å and 7.87 Å, respectively. Since the exchange interaction can take place only if the R_C is less than 5 Å, the energy transfer between doubly-doped samples should result from multipolar interaction.

Table S5 The lifetime of Ce^{3+} at 425 nm in GSBO:*x*Ce^{3+} (*x* = 0.01 - 0.05).

GSBO:*x*Ce^{3+}	*τ* (ns)
0.01	30.94
0.02	30.75
0.03	30.41
0.04	29.69
0.05	29.01

Table S6 The lifetime of Tb^{3+} at 542 nm in GSBO:*y*Tb^{3+} (*y* = 0.10 - 0.90).

GSBO:*y*Tb^{3+}	*τ* (ms)
0.10	2.52
0.30	2.40
0.50	2.32
0.70	2.02
0.90	1.68

Table S7 The lifetime of Sm^{3+} at 599 nm in GSBO:*z*Sm^{3+} (*z* = 0.01 - 0.11).

GSBO:*z*Sm^{3+}	τ (ms)
0.01	2.17
0.03	1.77
0.05	1.41
0.07	1.15
0.09	0.96

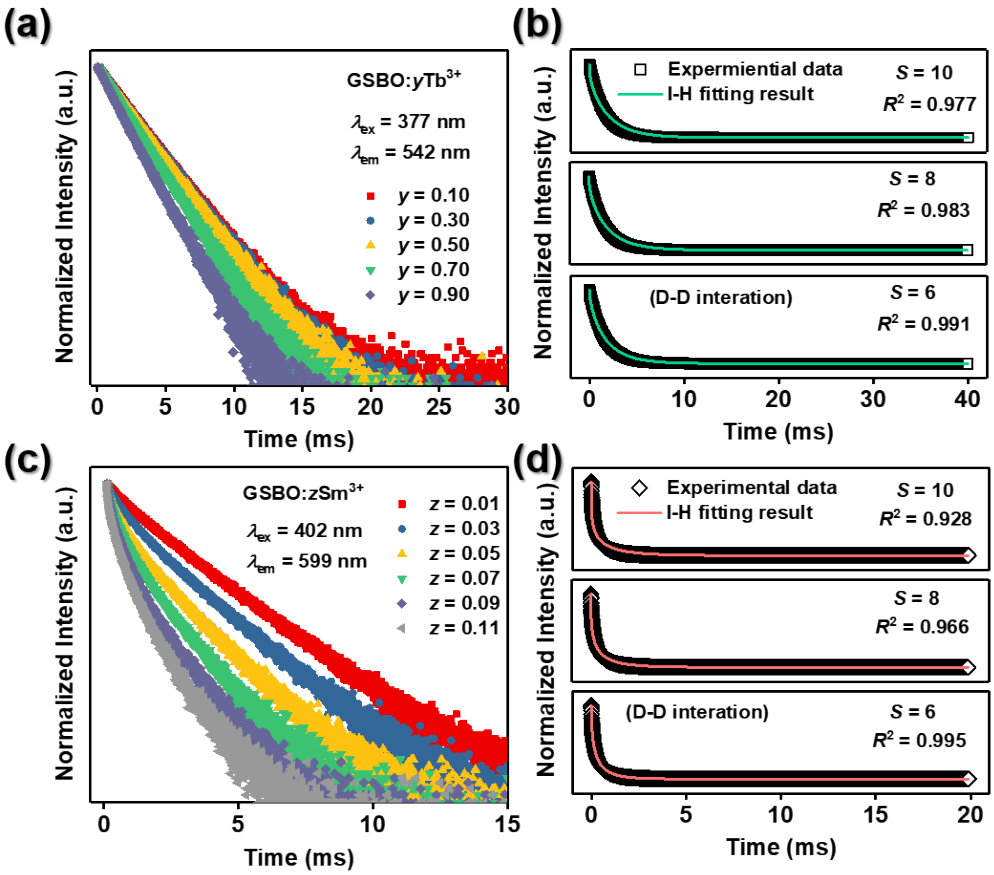

Fig. S5 The decay curves and the I-H fitting results of GSBO:yTb^{3+} and GSBO:zSm^{3+}.

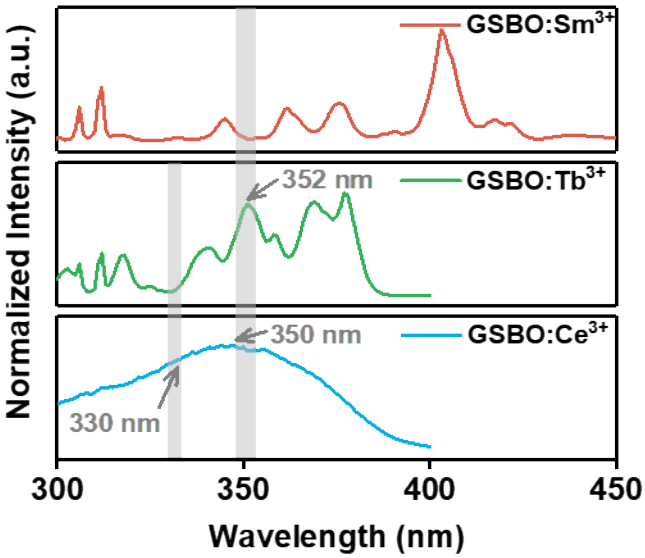

Fig. S6 The excitation spectra overlapping of GSBO:Ce^{3+}, GSBO:Tb^{3+} and GSBO:Sm^{3+}.

Table S8 The lifetime of Ce^{3+} at 425 nm in GSBO:0.03Ce^{3+},*y*Tb^{3+} (*y* = 0.04 - 0.20).

GSBO:0.03Ce^{3+},*y*Tb^{3+}	*τ* (ns)
0.04	30.08
0.08	29.94
0.12	29.84
0.16	29.05
0.20	28.13

Table S9 The lifetime of of Ce^{3+} at 425 nm in GSBO: 0.03Ce^{3+},*z*Sm^{3+} (*z* = 0.01 - 0.09).

GSBO:0.03Ce^{3+},*z*Sm^{3+}	*τ* (ns)
0.01	28.93
0.03	26.50
0.05	24.10
0.07	22.24
0.09	19.96

Table S10 The lifetime of Tb^{3+} at 542 nm in GSBO:0.50Tb^{3+},*z*Sm^{3+} (*z* = 0.01 - 0.09).

GSBO:0.50Tb^{3+},*z*Sm^{3+}	*τ* (ms)
0.01	2.29
0.03	2.11
0.05	1.93
0.07	1.80
0.09	1.69

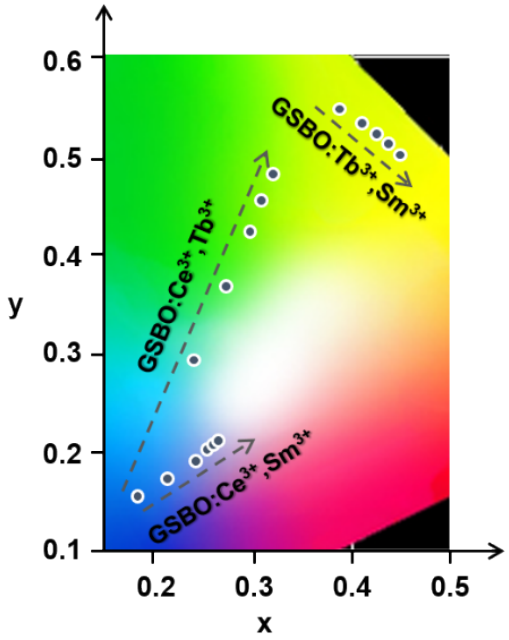

Fig. S7 The CIE chromaticity diagram of the doubly-doped phosphors.

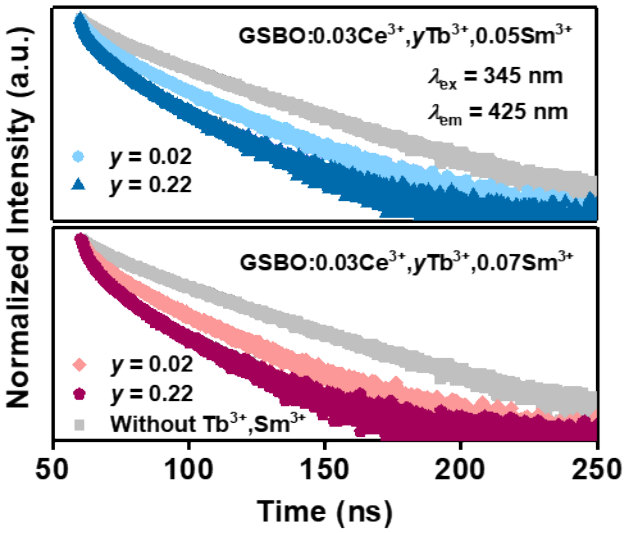

Fig. S8 The decay curves of GSBO:0.03Ce^{3+},yTb^{3+},0.05Sm^{3+} and GSBO:0.03Ce^{3+},*y*Tb^{3+},0.07Sm^{3+} samples (*y* = 0.02 and 0.22).

Table S11 The lifetime of Ce^{3+} at 425 nm in GSBO:0.03Ce^{3+},*y*Tb^{3+},0.05Sm^{3+} (*y* = 0.02 - 0.22).

GSBO:0.03Ce^{3+},*y*Tb^{3+},0.05Sm^{3+}	**τ (ns)**
0.02	24.84
0.06	24.51
0.10	24.35
0.14	23.78
0.18	23.11
0.22	22.51

Table S12 The lifetime of Ce^{3+} at 425 nm in GSBO:0.03Ce^{3+},*y*Tb^{3+},0.07Sm^{3+} (*y* = 0.02 - 0.22).

GSBO:0.03Ce^{3+},*y*Tb^{3+},0.07Sm^{3+}	**τ (ns)**
0.02	22.48
0.06	22.41
0.10	22.32
0.14	21.86
0.18	21.43
0.22	20.81

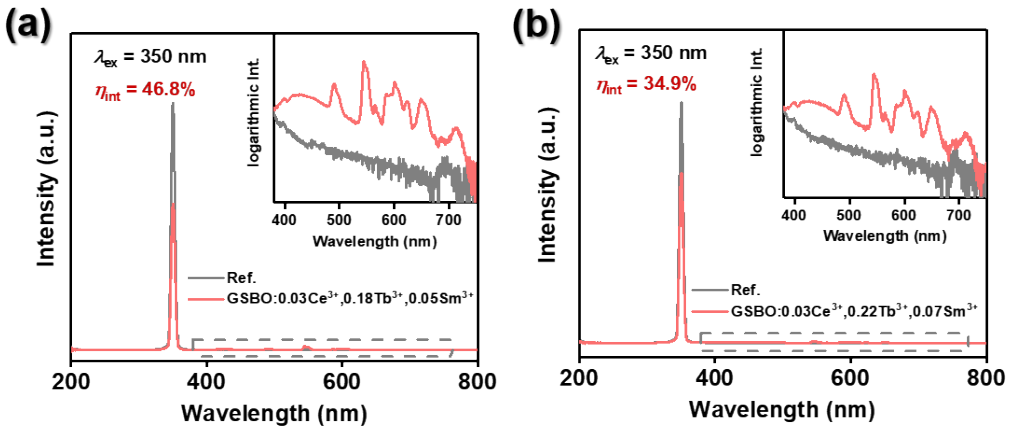

Fig. S9 The quantum efficiencies of GSBO:0.03Ce^{3+},0.18Tb^{3+},0.05Sm^{3+} and GSBO:0.03Ce^{3+},0.22Tb^{3+},0.07Sm^{3+}.

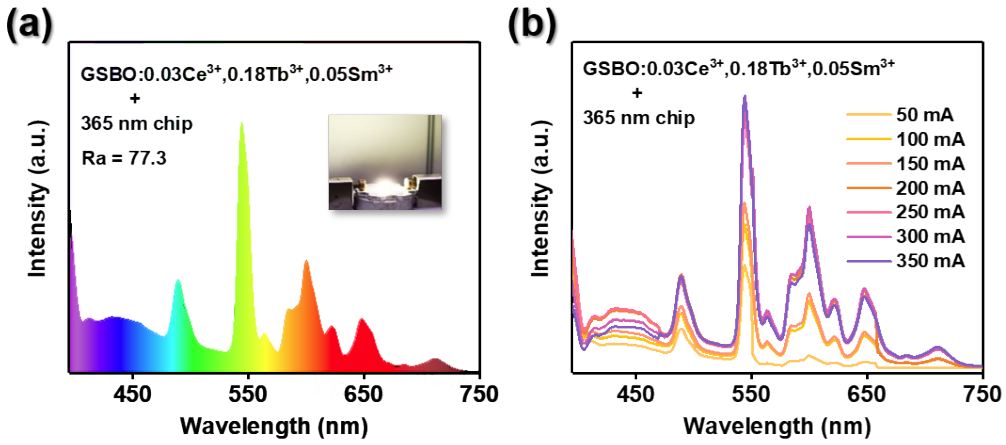

Fig. S10 (a) The EL spectrum of the WLED fabricated by GSBO:0.03Ce^{3+},0.18Tb^{3+},0.05Sm^{3+} with 365 nm LED chip and (b) the EL spectra of the as-fabricated WLED under various forward bias currents.

References

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