Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Structural calculations of $Gd(CO_3)OH$ luminescent nanospheres with the prospect for CL microscopic analysis and multi-color displays

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Measurement and characterizations

The phase identification was determined by X-ray diffraction (XRD, RIGAKU Inc., Japan, D/max2550 VB+) with Cu Kα radiation. The Thermogravimetric (TG) data were performed on a TGA-8120 instrument (RIGAKU Inc., Japan) in air from 35 to 900°C. The morphology and elemental information of the samples were measured by scanning electron microscope (SEM, FEI Helios Nanolab 600i) and transmission electron microscope (TEM, Titan G2 60-300). The DFT

calculation of the electronic band structure was conducted by using the Vienna ab initio simulation package (VASP) software. The generalized gradient approximation (GGA) were executed, which was expressed by Perdew-Burke-Ernzerhof (PBE).

The diffuse reflectance spectrum (DRS) was tested on the UV-VIS spectrophotometer (SHIMADZU, UV-2600) with $BaSO_4$ as the white background reference. The PL emission and excitation spectra were obtained by a FLS-920T fluorescence spectrophotometer with a 450 W Xe source. The luminescent decay curves were measured by the same system with the light source switched to microsecond flashlamp. The monitored excitation and emission wavelength were fixed at 380nm and 542nm respectively. The CL spectra were carried out by the Mp-Micro-S instrument (Horiba Jobin Yvon) with scanning electron microscopy (SEM, S-340, Hitachi, Japan).

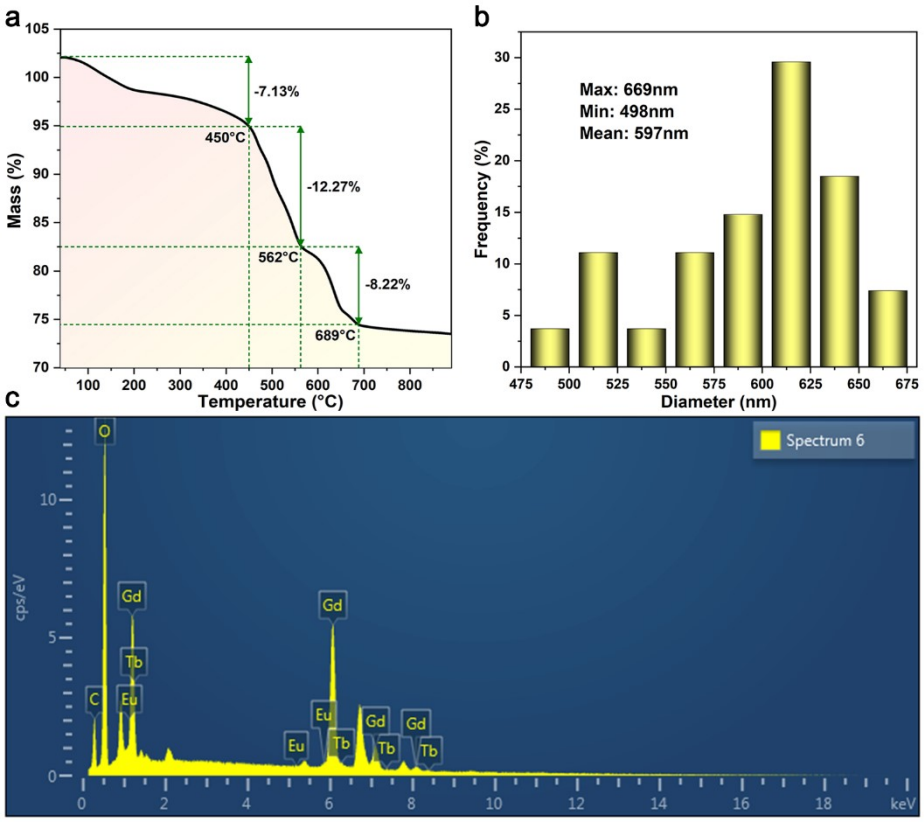

Figure S1 a The TG curve of $Gd(CO_3)OH$. **b** The frequency counts b and EDX spectrum **c** of the typical sample (3, 1)

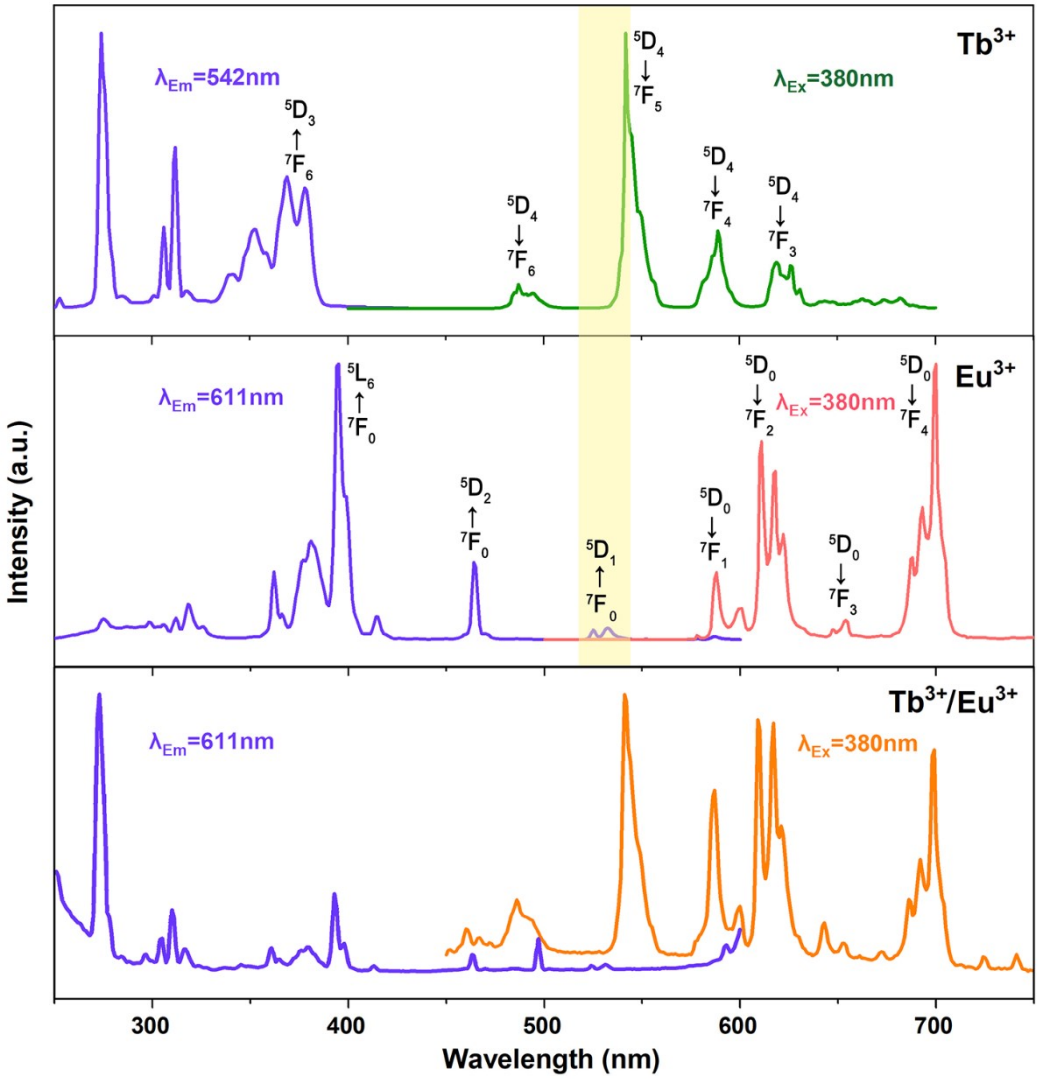

Figure S2 The PL excitation and emission spectra of the single and co-doped samples.

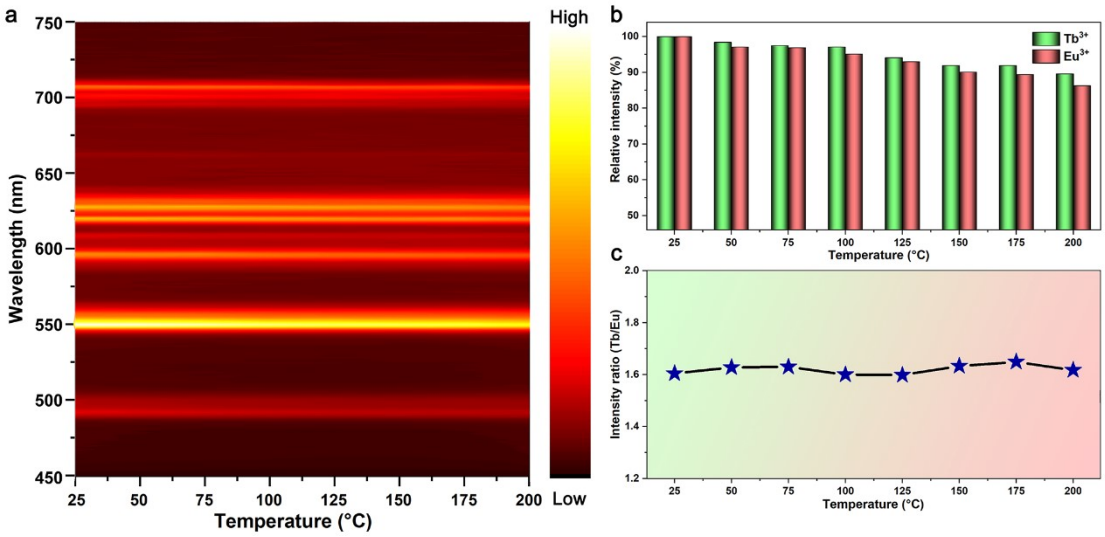

Figure S3 a The 2D temperature-dependent emission spectra of $Gd(CO_3)OH$: Tb^{3+}, Eu^{3+}(typical sample (3, 1)). **b** The relative intensities of Tb^{3+}, Eu^{3+} at increasing temperature. **c** The intensity ratio of Tb^{3+}/Eu^{3+} at increasing temperature.

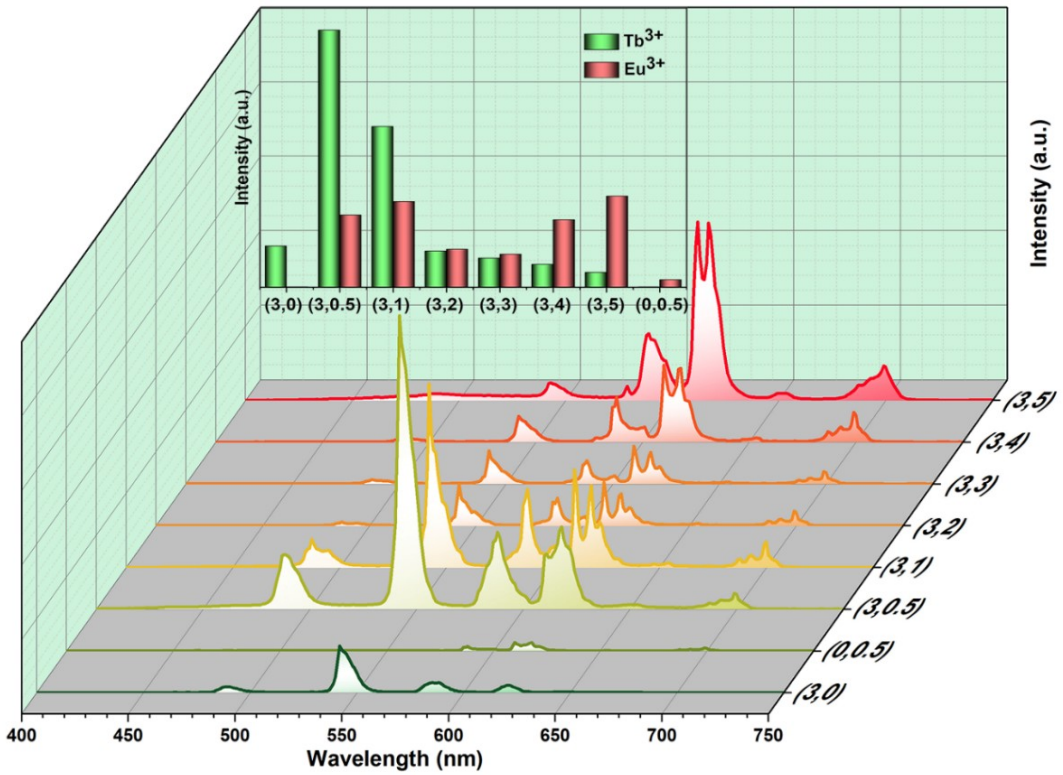

Figure S4 The original PL spectra of the series sample. The inset showed the intensities of Tb^{3+} and Eu^{3+}.

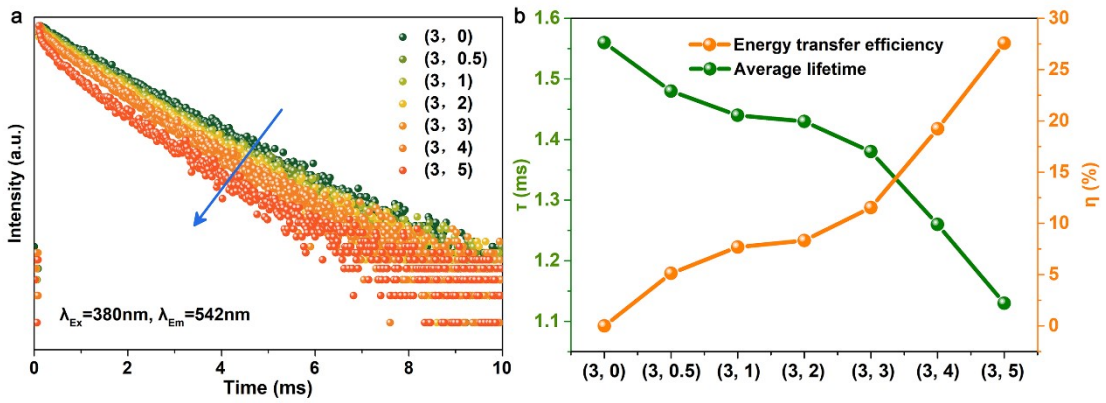

Figure S5 a The luminescence decay curves of the series sample. **b** The calculated average lifetime and energy transfer efficiency.

The luminescence decay curves of Tb^{3+} with the concentration of Eu^{3+} from 0% to 5% were tested in Figure S5a, in which gradually decreased lifetimes could be clearly viewed, indicating the energy loss of Tb^{3+} with the raise of Eu^{3+} content. The average lifetime τ of each sample could be conveniently calculated by the integral formula[1]:

$$\tau = \frac{\int_{\infty}^{0} I_D(t) t dt}{\int_{\infty}^{0} I_D(t) dt} \quad (1)$$

and converted to the energy transfer efficiency η_t by the formula[2]:

$$\eta_t = 1 - \frac{\tau}{\tau_0} \quad (2)$$

The results were plotted in Figure S5b. The average lifetime decreased from 1.56 to 1.13 ms, while the energy transfer efficiency reached the maximum of 27.56%. After logarithmic transformation, $\log[\ln(I_0/I)]$ is linear correlated to $\log(t)$

with a slope of 3/m. Hence the original decay curves were transformed and linear fitted in Figure 3e.

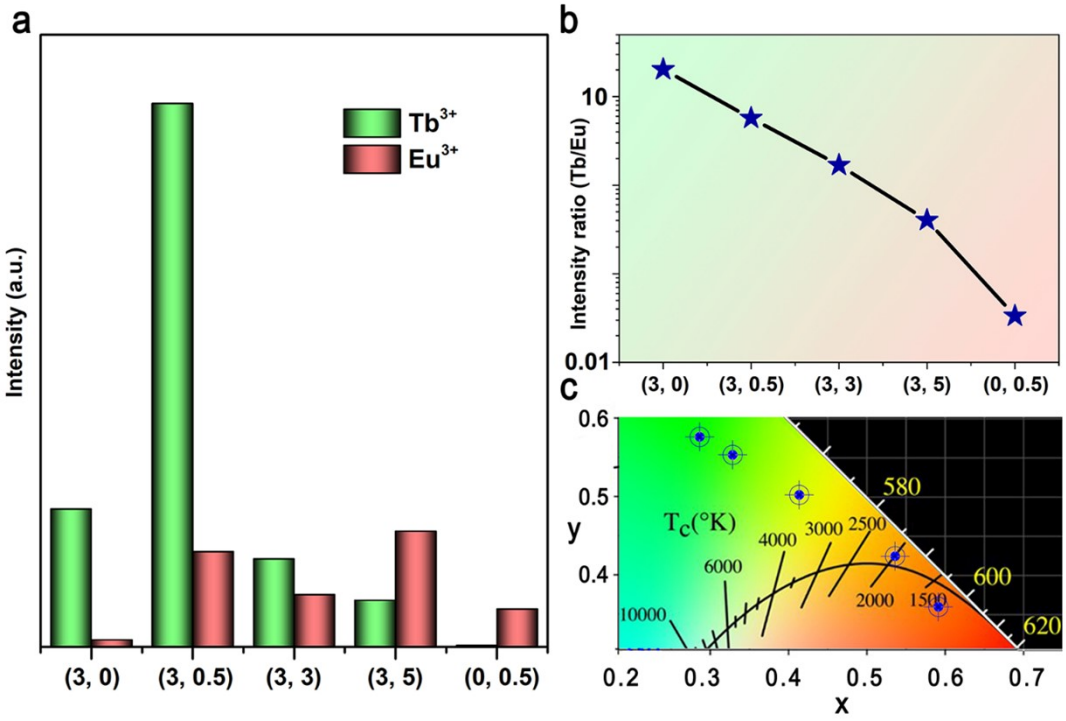

Figure S6 The relative luminescent intensity **a**, ratio **b** and chromaticity coordinates **c** of the selected series samples under electron beam radiation.

Table S1 Selected bond length of $Gd(CO_3)OH$.

Bonds	Length (Å)	Bonds	Length (Å)
Gd1-O1	2.56188(7)	C1-O1	1.24956(3)
Gd1-O1	2.62930(6)	C1-O3	1.35029(3)
Gd1-O2	2.37638(6)	H1-O1	1.84146(5)
Gd1-O2	2.44121(6)	H1-O2	1.51277(4)
Gd1-O3	2.47349(8)	H1-O2	1.68764(4)

Table S2 Element percentage of the sample (3, 1).

Element	Weight %	Atomic %
Gd	47.70	8.23
C	11.86	26.77
O	38.12	64.60
Tb	1.56	0.27
Eu	0.76	0.14

References:

[1] M. Jiao, N. Guo, W. Lü, Y. Jia, W. Lv, Q. Zhao, B. Shao, H. You, Tunable blue-green-emitting $Ba_3LaNa(PO_4)_3F$: Eu^{2+}, Tb^{3+} phosphor with energy transfer for near-UV white LEDs, *Inorg. Chem.,* 2013, **52**, 10340-10346.

[2] T. Zhou, L. Mei, Y. Zhang, L. Liao, H. Liu, Q. Guo, Color-tunable luminescence properties and energy transfer of Tb^{3+}/Sm^{3+} co-doped $Ca_9La(PO_4)_5(SiO_4)F_2$ phosphors, *Opt. Laser Technol.,* 2019, **111**, 191-195.