

Supporting Information

Morphology evolution, tunable down conversion luminescence and energy transfer of [CaY]F₂ crystals doped with Li⁺/Ce³⁺/Tb³⁺

Yini Mao,^a Zhiyi Wang,^a Rui Ye,^a Li Jiang,^a Shanshan Hu^{*a} and Jun Yang^{*a}

^aSchool of Chemistry and Chemical Engineering, Southwest University, No. 2 Tiansheng Road, Beibei District, Chongqing 400715, China.

E-mail: hushan3@swu.edu.cn and jyang@swu.edu.cn

Table S1. The emission and the absorption integral area values of the [CaY]F₂:0.1%Tb³⁺ phosphors with different morphology.

Contents of EDTA (g)	Morphology	Integral _(emission)	Integral _(absorption)
0	octahedral	9885.3694	1154.8755
0.35	cube	12861.02547	1129.0104
0.40	truncated cube	12247.3692	1138.6272
0.45	truncated octahedron	11232.0321	1152.9481
0.50	spherical	10695.98401	1139.526

Table S2. The relative quantum yields of [CaY]F₂:0.1%Tb³⁺ samples with different morphology at an excitation wavelength of 215 nm.

Contents of EDTA (g)	Morphology	$\lambda_{\text{ex}} = 215 \text{ nm}$
0	octahedral	46.07
0.35	cube	53.49
0.40	truncated cube	53.06
0.45	truncated octahedron	51.88
0.50	spherical	46.52

The relative quantum yield (RQY) can be calculated according to the following equation:¹⁻³

$$RQY = \frac{L_{\text{Sample}}}{E_{\text{Reference}} - E_{\text{Sample}}}$$

Where L_{Sample} is the emission integrals of samples, $E_{\text{Reference}}$ and E_{Sample} represent the absorption integrals of reference and samples. Use Hitachi F-7000 to measure the emission spectrum of the sample, use UV-2700 to measure the absorption spectrum of the sample and reference, respectively. Then integrate with the origin software to obtain the corresponding integral value as shown in Table S1.

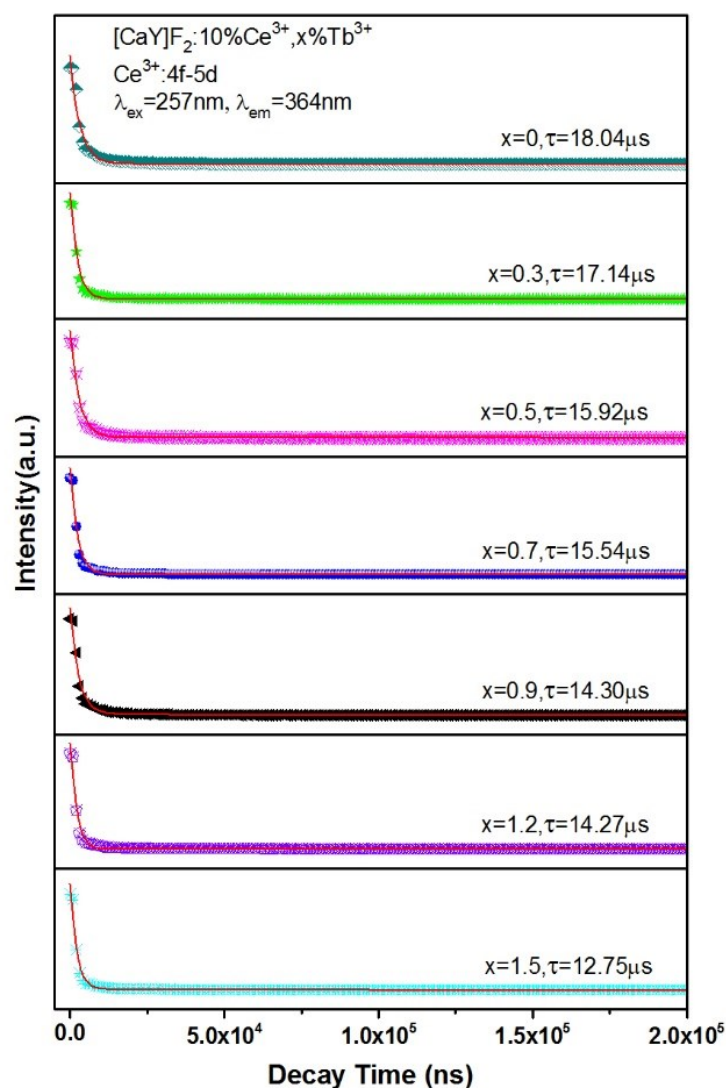


Figure S1. Luminescence decay curves of Ce^{3+} emission (4f-5d) in $[\text{CaY}]\text{F}_2:10\%\text{Ce}^{3+}$, $x\%\text{Tb}^{3+}$ ($x = 0, 0.3, 0.5, 0.7, 0.9, 1.2, 1.5$).

The luminescence decay curves of Ce^{3+} emission in $[\text{CaY}]\text{F}_2:10\%\text{Ce}^{3+}$, $x\%\text{Tb}^{3+}$ ($x = 0, 0.3, 0.5, 0.7, 0.9, 1.2, 1.5$) were measured to further understand the excited state dynamics of the energy transfer process. Fig. S1 presents the Ce^{3+} decay curves in $[\text{CaY}]\text{F}_2:10\%\text{Ce}^{3+}$, $x\%\text{Tb}^{3+}$, which are all well fitted into a second order exponential function as:¹

$$I(t) = I_0 + A_1 \exp(-t / \tau_1) + A_2 \exp(-t / \tau_2)$$

Where $I(t)$ represents the emission intensity, τ_1 and τ_2 respectively refer to the rapid and slow decay time of the exponential function, A_1 and A_2 are constants. The

average decay time can be calculated by the following formula:^{3, 4}

$$\tau = (A_1\tau_1^2 + A_2\tau_2^2) / (A_1\tau_1 + A_2\tau_2)$$

As shown in Fig. S1, the average decay times of [CaY]F₂:10%Ce³⁺, x%Tb³⁺ (x = 0, 0.3, 0.5, 0.7, 0.9, 1.2, 1.5) were calculated to be 18.04, 17.14, 15.92, 15.54, 14.30, 13.27 and 12.75 μ s, respectively. Obviously, the decay time of Ce³⁺ decreases monotonically with the increase of the Tb³⁺ concentration, which strongly proves the fact that the energy has been successfully transferred from Ce³⁺ to Tb³⁺ and reasonably explains the phenomenon that the emission peak of Tb³⁺ obtained under excitation at 257 nm is much stronger than that of 215 nm.

- [1] Z. Jia, X. L. Zhang, X. Y. Hua, Y. Dong, H. L. Li, C. Q. Feng, Y. G. Wang, M. J. Xia, *Journal of Alloys and Compounds*, 2020, 844, 155875.
- [2] H. Guo, X. Y. Huang, *Journal of Alloys and Compounds*, 2018, 764, 809-814.
- [3] L. M. Teng, W. N. Zhang, W. P. Chen, J. K. Cao, X. Y. Sun, H. Guo, *Ceramics International*, 2020, 46, 10718–10722.
- [4] W. P. Xia, Y. F. Zhang, J. Xiong, S. S. Hu, J. Yu, Y. F. Zhang, Y. X. Wang and J. Yang, *CrystEngComm*, 2019, 21, 339-347.
- [5] C. Li, H. W. Zheng, H. W. Wei, S. J. Qiu, L. Xu, X. M. Wang and H. Jiao, *Dalton Trans.*, 2018, 47, 6860-6867.