Supporting Information

Unique excitation power density and pulse width dependent multicolor upconversion emissions of Y₂Mo₄O₁₅:Yb³⁺,Ho³⁺ for anti-counterfeiting and information encryption applications

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1. Photoluminescence quantum yield (PLQY):

The absolute PLQY value is defined as the ratio of the number of photons emitted to the number of photons absorbed, which can be expressed in the following formula:

$$\Phi = \frac{\int L_S}{\int E_R - \int E_S}$$

where $\int E_R$ represents the integral area of the excitation spectrum of BaSO₄ in the integrating sphere, $\int E_S$ represents the integral area of the excitation spectrum of the sample in the integrating sphere, and $\int L_S$ represents the integral area of the emission spectrum.

Table S1 Absolute PLQY of $Y_2Mo_4O_{15}$:40%Yb³⁺,2%Ho³⁺ under excitation of differentpower densities

Power density (W/cm ²)	PLQY (%)
5	0.21
20	0.52
50	0.65
100	0.71

2. Camera parameters

The photos in Fig.2, S2, S3 and S6 were taken with a microscope, and the microscope camera setting are as follows: The exposure time and ISO are 0.46 s and 3500, 0.28 s and 3200, 0.20 s and 2900, 0.18 s and 2500, 0.11 s and 2200, 0.07 s and 1900 in the insets photographs from Fig.2a to 2f, respectively. The exposure time and ISO are 0.43 s and 5800, 0.39 s and 3700, 0.36 s and 4000, 0.34 s and 3200, 0.31 s and 2700, 0.29 s and 2300 in the insets photographs from Fig.S2a to S2f, respectively. The exposure time and ISO are 0.38 s and 4700, 0.36 s and 4200, 0.33 s and 4000, 0.29 s and 3400, 0.25 s and 2900, 0.22 s and 2600 in the insets photographs from Fig.S3a to S3f, respectively. The exposure time and ISO are 0.40 s and 4900, 0.37 s and 4500, 0.35 s and 4200 in the insets photographs from Fig.S6a to S6c, respectively. Besides, we took other photos (Fig. 3,5) using iPhone 13. As the power density of 980 nm c.w. laser increased from 0.7 to 93 W/cm², the exposure time and ISO are 0.50 s and 3200, 0.15 s and 1700, 0.03 s and 500, respectively (Fig. 3). As the pulse width of the 980 nm pulsed laser decreased from 10 to 0.1 ms, the exposure time and ISO are 0.02s and 320, 0.18s and 2100, 0.48 and 3000, respectively (Fig. 5). And all of the photos are automatic white balance.



Fig. S1 Optimization of lanthanide ion doping concentration in Y₂Mo₄O₁₅ material.



Fig. S2 Upconversion emission spectra of $Y_2Mo_4O_{15}$:40%Yb³⁺,2%Er³⁺ microcrystals under different excitation power densities. From a to f, the excitation power densities of 980 nm are 0.5, 2.0, 5.0, 20, 50, 100 W/cm², respectively. The corresponding microfluorescence photographs are illustrated in the inset.



Fig. S3 Upconversion emission spectra of $Y_2Mo_4O_{15}$:40%Yb³⁺,2%Tm³⁺ microcrystals under different excitation power densities. From a to f, the excitation power densities of 980 nm are 0.5, 2.0, 5.0, 20, 50, 100 W/cm², respectively. The corresponding microfluorescence photographs are illustrated in the inset.



Fig. S4 Upconversion emission spectra of NaYF₄:40%Yb³⁺,2%Ho³⁺ microcrystals under different excitation power densities. From a to f, the excitation power densities of 980 nm are 0.5, 2.0, 5.0, 20, 50, 100 W/cm², respectively.



Fig. S5 R/G ratio of NaYF₄:40%Yb³⁺,2%Ho³⁺ microcrystals under different excitation power densities.



Fig. S6 Upconversion emission spectra of $NaYF_4:Yb^{3+}$,Ho³⁺ microcrystals under different pulse width excitation. The pulse width of 980 nm laser from left to right is 10, 0.5 and 0.1 ms, respectively. The corresponding microfluorescence photographs are illustrated in the inset.



Fig. S7 The measured lifetime of the ${}^{5}I_{6}$ state in NaYF₄ and Y₂Mo₄O₁₅ under the excitation of 640 nm.



Fig. S8 Upconversion photoluminescence (PL) decay curves of green emission and red emission in a) $Y_2Mo_4O_{15}$:Yb³⁺,Ho³⁺ and b) NaYF₄:Yb³⁺,Ho³⁺, respectively. The rising and decay times of red emission in $Y_2Mo_4O_{15}$:Yb³⁺,Ho³⁺ is longer than the green one. However, the rising and decay times of both red and green emission in NaYF₄:Yb³⁺,Ho³⁺ are almost the same

Materials	phonon energy (cm ⁻¹)	Ref.
KPb ₂ Br ₅	138	1
RbPb ₂ Br ₅	141	2
$BaCl_2$	200	3
Cs ₂ AgBiCl ₆	280	4
$Cs_2AgInCl_6$	300	5
KLaF4	262	6
NaYF ₄	360	7
BaF_2	385	8
CaF_2	400	9
YOF	482	10
Y_2O_3	582	11
YAlO ₃	570	12
YNbO ₄	700	13
Y ₃ Al ₅ O ₁₂	857	14
$Y_2Mo_4O_{15}$	1039	This work

Table S2 Comparison of the phonon energy for different materials

References

- 1 U. Hömmerich, E. E. Nyein and S. B. Trivedi, J. Lumin., 2005, 113, 100-108.
- 2 K. Rademaker, S. A. Payne, G. Huber, L. I. Isaenko and E. Osiac, *J. Opt. Soc. Am. B*, 2005, **22**, 2610.
- 3 H. Jin, Z. Mo, X. Zhang, L. Yuan, M. Yan and L. Li, J. Lumin., 2016, 175, 187-192.
- 4 Y. Pei, D. Tu, C. Li, S. Han, Z. Xie, F. Wen, L. Wang and X. Chen, *Angew. Chem. Int. Ed. Engl.*, 2022, **61**, e202205276.
- 5 H. Siddique, Z. Xu, X. Li, S. Saeed, W. Liang, X. Wang, C. Gao, R. Dai, Z. Wang and Z. Zhang, *J. Phys. Chem. Lett.*, 2020, **11**, 9572-9578.
- 6 S. Ahmad, G. V. Prakash and R. Nagarajan, Inorg. Chem., 2012, 51, 12748-12754.
- 7 M. K. Jin, J. M. Xiang, Y. H. Chen, C. H. Chen, H. Suo, Z. Y. Zhang, J. S. Sun, X.
 Q. Zhao and C. F. Guo, *J. Lumin.*, 2022, 244 118692.
- 8 C. Hu, L. Lei, E. Liu, Z. Lu and S. Xu, J. Lumin, 2022, 247, 118905.
- 9 C. L. Hu, L. Lei, Y. B. Wang and S. Q. Xu, J. Lumin, 2022, 252 119357.
- 10 H. Suo, C. Guo, J. Zheng, B. Zhou, C. Ma, X. Zhao, T. Li, P. Guo and E. M. Goldys, ACS Appl. Mater. Interfaces, 2016, 8, 30312-30319.
- 11 M. Jin, J. Xiang, Y. Chen, C. Chen, H. Suo, Z. Zhang, J. Sun, X. Zhao and C. Guo, *J. Lumin*, 2022, **244**, 118692.
- 12 H. Kawahara, K. Fujioka and H. Furuse, Japanese J. Appl. Phys., 2020, 59, 112004.
- 13 Y. Tian, Y. Tian, P. Huang, L. Wang, Q. Shi and C. e. Cui, *Chem. Eng. J.*, 2016, 297, 26-34.
- 14 W. Mu, Y. Yin, Z. Jia, L. Wang, J. Sun, M. Wang, C. Tang, Q. Hu, Z. Gao, J. Zhang, N. Lin, S. Veronesi, Z. Wang, X. Zhao and X. Tao, *RSC Adv.*, 2017, 7, 21815-21819.