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Supporting Information

Photon Upconversion Afterglow Material toward Visualized Information Coding/Decoding

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Supplementary Experimental

Synthesis of ABF₃: Yb³⁺, Mn²⁺ (A=Na, K, Rb;B=Cd, Zn, Mg) by solvothermal method.

Materials

The raw materials $CdC_4H_6O_4\cdot 4H_2O$ (99.99%), $ZnC_4H_6O_4\cdot 2H_2O$ (99.99%), $MgC_4H_6O_4\cdot 4H_2O$ (99.99%), $MnC_4H_6O_4\cdot 4H_2O$ (99.99%), KF (99.9%), NaF (99.99%), RbF (99.9%) were purchased from Aladdin Industrial Corporation. Yb₂O₃ (99.998%) were purchased from Alfa Aesar Reagent Company. Oleic acid ($C_{18}H_{34}O_2$, 99%) was purchased from Sigma Alaserrich. Nitric acid (HNO_3 , AR) and absolute ethanol were obtained from Guangzhou Chemical Reagent Co., Ltd (China). Yb(NO_3)₃ was obtained by dissolving Yb₂O₃ in concentrated nitric acid. All chemicals were used as received without further purification.

Synthesis procedure

In a typical process to synthesize KZnF₃:2%Yb³⁺, 5%Mn²⁺, 5 ml oleic acid and 15 ml absolute ethanol were mixed together under agitation. Then 4.725 mmol ZnC₄H₆O₄·4H₂O, 0.25 mmol MnC₄H₆O₄·4H₂O and 2 ml Yb(NO₃)₃ solution (0.05 mol/L) were added to the above solution in turn under stirring for 20 minutes. Finally, 20 mmol KF was added into the solution. After vigorous agitation for another 20 minutes, the mixture was transferred into a 50 ml autoclave, sealed and heated at 220°C for 20 h. After the reaction, the system was cooled to room temperature naturally, and the products were collected and centrifuged several times with distilled water and absolute ethanol, and finally dried at 70°C for several hours. Other samples (RbCdF₃:2%Yb³⁺, 5%Mn²⁺; KCdF₃:2%Yb³⁺, 5%Mn²⁺; NaMgF₃:xYb³⁺, *y* (*x*=0.5,2%, *y*=5-60%)) were synthesized by the similar procedure.

Synthesis of RbCaF₃: 5%Yb³⁺, 10%Mn²⁺ by the high temperature solid state method.

The raw materials were Yb_2O_3 (99.998%), MnCO₃ (99.95%), RbF (99.9%), CaF₂ (99.99%), NH₄HF₂ (98%). Yb_2O_3 were purchased from Alfa Aesar Reagent Company (Shanghai, China), and other materials were supplied by Aladdin Industrial Corporation (Shanghai, China). All chemicals were used as received without further purification. The RbCaF₃: 5%Yb³⁺, 10%Mn²⁺were synthesized by the similar procedure with that of KCaF₃: Yb³⁺,Mn²⁺.

Theoretical Calculations. To evaluate the Mn²⁺ distribution in KCaF₃:Mn²⁺ (NaMgF₃), a $2 \times 2 \times 2$ KCaF₃ (NaMgF₃) supercell was constructed. As two Ca²⁺(Mg²⁺) ions are replaced by two Mn²⁺ ions in the optimized $2 \times 2 \times 2$ KCaF₃(NaMgF₃) supercell, there were 15 different configurations. The cutoff energy E_{cut} and K-point mesh were set as 520 eV with a $1 \times 1 \times 1$ Monkhorst-Pack grid, which are enough for energy convergence. The convergence criterion for the electronic energy was 10^{-4} eV and the structures were relaxed until the Hellmann–Feynman forces were less than 0.02 eV Å⁻¹.

formula	KCaF ₃	KCaF ₃ :5%Yb ³⁺ , 5%Mn ²⁺
space group	Pnma(62)	Pnma(62)
a (Å)	6.20288(4)	6.16324(9)
b (Å)	8.74714(6)	8.71737(12)
c (Å)	6.15387(5)	6.16072(9)
α=β=γ (°)	90	90
Z	4	4
V (Å ³)	333.894(4)	330.999(8)
R _{wp} (%)	6.79	4.94
R _p (%)	4.77	3.64
χ^2	3.620	2.567

Table S1 Rietveld refinement data for $KCaF_3$ and $KCaF_3$:5%Yb³⁺, 5%Mn²⁺

Note: The refinements are stable and give low R-factors.

Table S2 Atomic coordinates and isotropic temperature parameters (Å²) for KCaF₃ and KCaF₃:5%Yb³⁺, 5%Mn²⁺

	ato	х	у	Z	Occ.	Wyck	100*U _{iso}
	m					•	
	K1	0.02641(19)	1/4	0.49460(32)	1	4c	3.416(25)
KCaF.	Ca1	0	0	0	1	4a	1.526(17)
Keur 3	F1	-0.02285(45)	1/4	0.93630(39)	1	4c	1.61(8)
	F2	0.28958(32)	0.03960(23)	0.21074(32)	1	8d	2.89(6)
	K1	0.0108(5)	1/4	0.4988(13)	1	4c	3.705(27)
	Ca1	0	0	0	0.9	4a	1.609(17)
KCaF₃:5%Yb ³⁺ ,	F1	-0.0396(9)	1/4	0.9214(6)	1	4c	3.55(15)
5%Mn ²⁺	F2	0.2844(5)	0.02283(29)	0.2172(5)	1	8d	2.10(6)
	Yb1	0	0	0	0.05	4a	1.609(17)
	Mn1	0	0	0	0.05	4a	1.609(17)

bond	KCaF ₃	bond	KCaF ₃ :5%Yb ³⁺ , 5%Mn ²⁺
Ca1-F1	2.2262(5)	Ca1/Yb1/Mn1-F1	2.2459(11)
Ca1-F1	2.2262(5)	Ca1/Yb1/Mn1-F1	2.2459(11)
Ca1-F2	2.2424(20)	Ca1/Yb1/Mn1-F2	2.2141(29)
Ca1-F2	2.2344(20)	Ca1/Yb1/Mn1-F2	2.2001(29)
Ca1-F2	2.2424(20)	Ca1/Yb1/Mn1-F2	2.2141(29)
Ca1-F2	2.2344(20)	Ca1/Yb1/Mn1-F2	2.2001(29)

Table S3 Selected bond distances for $KCaF_3$ and $KCaF_3{:}5\%Yb^{3+}\text{, }5\%Mn^{2+}$

angle	KCaF ₃	angle	KCaF ₃ :5%Yb ³⁺ , 5%Mn ²⁺
F1-Ca1-F1	180.000(0)	F1-Ca1/Yb1/Mn1-F1	180.000(0)
F1-Ca1-F2	90.06(9)	F1-Ca1/Yb1/Mn1-F2	97.43(14)
F1-Ca1-F2	92.82(8)	F1-Ca1/Yb1/Mn1-F2	89.01(14)
F1-Ca1-F2	89.94(9)	F1-Ca1/Yb1/Mn1-F2	82.57(14)
F1-Ca1-F2	87.18(8)	F1-Ca1/Yb1/Mn1-F2	90.99(14)
F1-Ca1-F2	89.94(9)	F1-Ca1/Yb1/Mn1-F2	82.57(14)
F1-Ca1-F2	87.18(8)	F1-Ca1/Yb1/Mn1-F2	90.99(14)
F1-Ca1-F2	90.06(9)	F1-Ca1/Yb1/Mn1-F2	97.43(14)
F1-Ca1-F2	92.82(8)	F1-Ca1/Yb1/Mn1-F2	89.01(14)
F2-Ca1-F2	90.961(22)	F2-Ca1/Yb1/Mn1-F2	90.491(23)
F2-Ca1-F2	180.000(0)	F2-Ca1/Yb1/Mn1-F2	180.000(0)
F2-Ca1-F2	83.039(22)	F2-Ca1/Yb1/Mn1-F2	89.509(23)
F2-Ca1-F2	83.039(22)	F2-Ca1/Yb1/Mn1-F2	89.509(23)
F2-Ca1-F2	180.000(0)	F2-Ca1/Yb1/Mn1-F2	180.000(0)
F2-Ca1-F2	90.961(22)	F2-Ca1/Yb1/Mn1-F2	90.491(23)

Table S4 Selected bond angles for KCaF₃ and KCaF₃:5%Yb³⁺, 5%Mn²⁺

Table S5 Average bond lengths (Å) and distortion index of CaF_6 octahedron in $KCaF_3$

octahedron	average bond lengths (Å)	distortion index
CaF ₆	2.2343	0.002427

The distortion index of the CaF₆ octahedron is calculated by using the following equation:

$$D = \frac{1}{n} \sum_{i=1}^{n} \frac{|l_i - l_{av}|}{l_{av}}$$

Where I_i is the distance from the central atom to the *i*th coordinating atom and I_{av} is the average bond length.

Model	KCaF ₃		$NaMgF_3$	NaMgF ₃	
model	Mn1-Mn2 distance (Å)	E_t (eV)	Mn1-Mn2 distance (Å)	E_t (eV)	
M1	4.2666	-833.8325	3.8185	-797.7180	
M2	4.2395	-833.8370	3.8168	-797.7080	
M3	6.1675	-833.8365	5.4433	-797.6124	
M4	6.2703	-833.8270	5.3633	-797.6159	
M5	7.6494	-833.7777	6.5986	-797.6145	
M6	8.7809	-833.8006	5.4408	-797.6154	
M7	9.8147	-833.8348	5.5291	-797.6149	
M8	6.1742	-833.8415	6.7340	-797.6136	
M9	10.7904	-833.8251	7.7027	-797.6095	
M10	6.1796	-833.8504	8.6091	-797.6162	
M11	7.5677	-833.7810	7.6981	-797.6136	
M12	8.8002	-833.7806	8.6042	-797.6152	
M13	9.82540	-833.8314	9.3798	-797.6159	
M14	10.7428	-833.8341	9.4732	-797.6149	
M15	12.4292	-833.8113	10.8933	-797.6125	

Table S6 The Mn1-Mn2 distance and total energy (E_t) of the fifteen proposed substitution models for $2 \times 2 \times 2$ supercell of KCaF₃ and NaMgF₃ with two Ca²⁺ or Mg²⁺ ions replaced by two Mn²⁺ ions.

Table S7 Calculated formation energies for different occupation configurations when Ca^{2+} is substituted by Yb³⁺ ion

No.	occupation configuration	<i>E_f</i> (eV)
i	$Yb_{Ca}^{g} - V_{K}'$	5.4760-5.4824
ii	$2Yb_{Ca}^{g}$ - V_{Ca}''	11.3085-11.5115
iii	Yb_{Ca}^{g} - O_{F}'	4.0921-4.1443

KCaF ₃ :5%Yb ³⁺ , xMn ²⁺	τ _{uc} /ms
1%	31.88
3%	36.64
5%	40.31
10%	36.15
15%	19.60
20%	10.25
30%	6.71

Table S8 The average UC lifetimes of KCaF₃:5%Yb³⁺, *x*Mn²⁺ (*x*=1-30%)



Fig. S1 (a) TEM microgragh, (b) selected area electron diffraction (SAED) pattern, (c) high resolution TEM image and (d) HAADF-STEM and the mapping distribution of elements in KCaF₃:5%Yb³⁺,5%Mn²⁺.



Fig. S2 XRD Rietveld refinement for $KCaF_3:5\%Yb^{3+}$, $5\%Mn^{2+}$, showing the observed (Black crosses) and calculated (red line) XRD profiles, and the difference between them (blue line). Bragg reflection positions are marked with green vertical bars.



Fig. S3 Chromaticity coordinates and color purity of the as-synthesized yellow phosphor $KCaF_3:5\%Yb^{3+},5\%Mn^{2+}$.

The color purity of phosphor is an important feature in evaluating its chromaticity property, which can be calculated using the following equation¹:

color purity=
$$\frac{\sqrt{(x-x_i)^2+(y-y_i)^2}}{\sqrt{(x_d-x_i)^2+(y_d-y_i)^2}} \times 100\%$$

where (x, y) is the color coordinates of the phosphor, (x_i , y_i) is the CIE of an equal-energy illuminant with a value of (0.3333, 0.3333), and (x_d , y_d) is the chromaticity coordinates corresponding to the dominant wavelength of the light source.



Fig. S4 Pump power dependent UC emission spectra of $KCaF_3$: 5%Yb³⁺, 10%Mn²⁺ upon excitation of a 940 nm LED with a power of 240-700 mW. The insets shows the corresponding double-logarithmic plots of the UC emission intensity versus pump power as well as the 940 nm LED and its luminescence images.



Fig. S5 (a) XRD patterns, (b) UC emission spectra and (c) the corresponding relative UC intensity, (d) the excitation/emission spectra of $ABF_3:xYb^{3+},yMn^{2+}$ (A=Na, K, Rb; B=Ca, Cd, Zn, Mg; x,y=5%,10% for Rb/KCaF₃ prepared by the high temperature solid state method, x,y=2%,5% for other samples prepared by the solvothermal method).



Fig. S6 (a) XRD patterns of NaMgF₃:0.5%Yb³⁺, xMn²⁺ (x=5-60%) and (b) the corresponding UC emission spectra upon excitation of 980 nm laser.







M13





a

С



Fig. S7 Fifteen possible substitution models for two Mn^{2+} ions substitute two Ca^{2+} ions in a $2 \times 2 \times 2$ supercell of KCaF₃.

M14

M15



Fig. S8 Fifteen possible substitution models for two Mn^{2+} ions substitute two Mg^{2+} ions in a $2 \times 2 \times 2$ supercell of NaMgF₃.



Fig. S9 Pump power dependent UC emission spectra of $KCaF_3$: 5%Yb³⁺, 10%Mn²⁺ with power varying from 94 to 446 mW. The inset shows the corresponding double-logarithmic plots of the UC emission intensity versus pump power.



Fig. S10 UC emission spectra of KCaF₃: 5%Yb³⁺, 10%Mn²⁺ and KCaF₃: 5%Yb³⁺, 2%Eu³⁺ upon excitation with a 980 nm laser.



Fig. S11 (a) XPS spectra of $KCaF_3$: 5%Yb³⁺, 10%Mn²⁺; (b) high-resolution XPS of Yb 4d.



Fig. S12 Three possible substitution models for Mn^{2+} ion substitutes Ca^{2+} ion based on the third $Yb_{Ca}^{g} - O'_{F}$ configuration and the corresponding formation energy.



Fig. S13 (a) Temperature-dependent UC emission spectra of $RbCaF_3$: 5%Yb³⁺, 10%Mn²⁺ and (b) the corresponding integrated UC emission intensity.



Fig. S14 Temperature-dependent luminescent photographs of KCaF₃: 5%Yb³⁺, 10%Mn²⁺ upon dynamic radiation of 980 nm laser. (power density, ~13.41 W cm⁻², moving speed, ~8.72 cm s⁻¹). The scale bar is 5 mm.



Fig. S15 UC emission spectra of the commercial UC phosphors and the corresponding UC decay curves.



Fig. S16 (a) UC emission spectra of luminescent inks containing $KCaF_3$: 5%Yb³⁺, 10%Mn²⁺ as well as different commercial pigments, and (b) the corresponding UC decay curves.



Fig. S17 (a) Photograph of the UC luminescence of a wooden bottle cap printed with $KCaF_3:5\%Yb^{3+},10\%Mn^{2+}$ luminescent ink upon dynamic irradiation of the commercial 980 nm laser pen with a maximum power of 0.1 W ($\omega \approx 200$ rmp). (b) The Photograph of the 980 nm laser pen. The scale bar is 10 mm.



Fig. S18 Photographs of the afterglow of the carboards printed with luminecent inks containing different commercial persistent phoshors (purchased from Luming technology group co. LTD, Dalian, China.) after stopage of the excitation of 375 nm laser for 2 seconds.(a-d) the afterglow after the first excitation,(e-h) the afterglow after the second excitation (30 seconds later than the first excitation).

8.72 cm/s		
		-
8.10 cm/s		
6.23 cm/s		
5.61 cm/s	2 ¹ cm	<mark>'0</mark>

Fig. S19 Velocity-dependent luminescent photographs of KCaF₃: 5%Yb³⁺, 10%Mn²⁺ upon dynamic radiation of 980 nm laser. (power density, ~13.41 W cm⁻², moving speed, ~5.61-8.72 cm s⁻¹). The scale bar is 5 mm.

References:

1 J. Zheng, Q. Cheng, S. Wu, Z. Guo, Y. Zhuang, Y. Li and C. Chen, J. Mater. Chem. C., 2015, **3**, 11219.