

## Supporting Information (SI)

# A novel red phosphor $\text{Cs}_2\text{NaGaF}_6:\text{Mn}^{4+}$ with ultra-strong zero-phonon lines and long wavelength phonon sidebands for high-quality WLEDs

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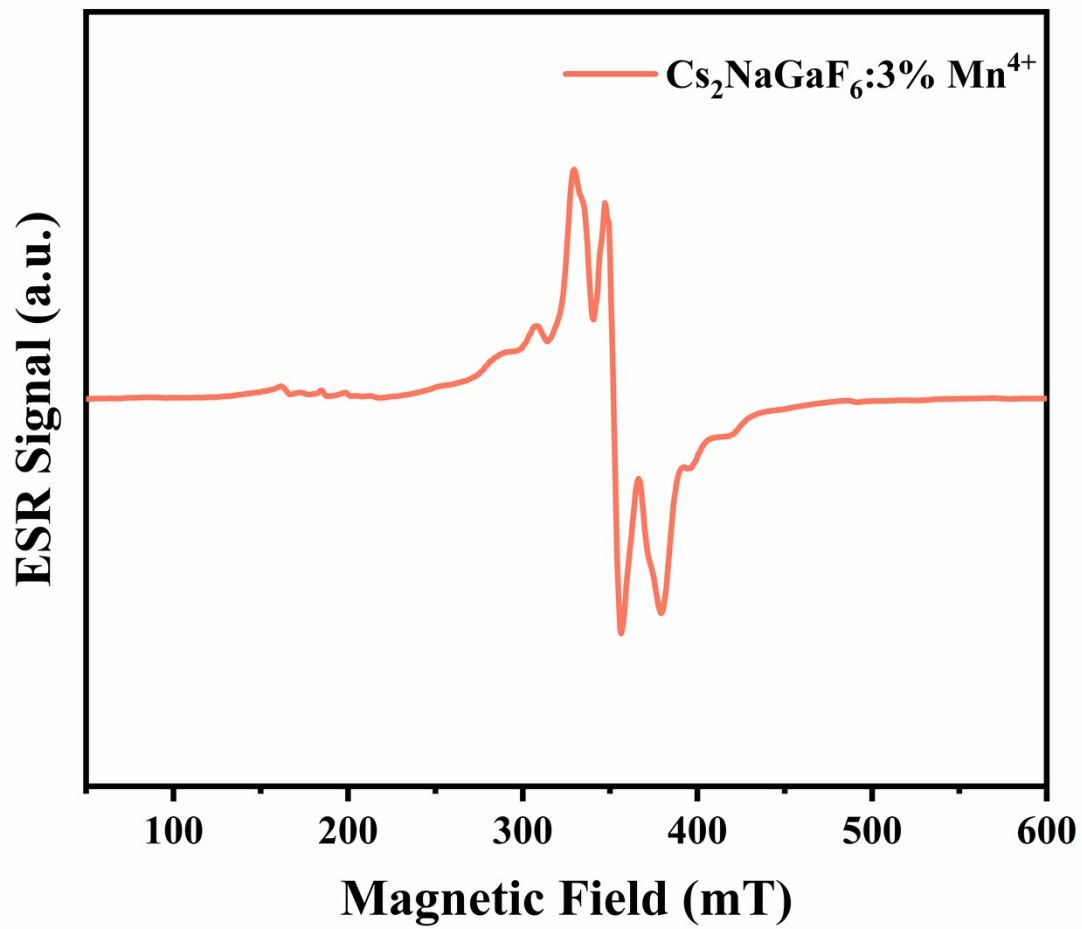
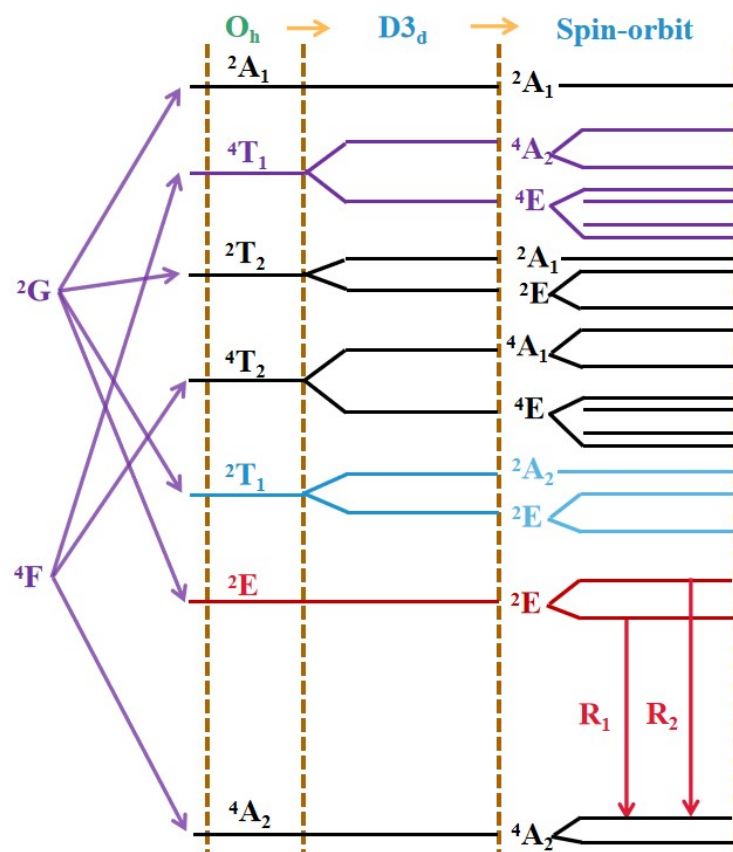


Fig. S1 EPR spectra of Cs<sub>2</sub>NaGaF<sub>6</sub>:3%Mn<sup>4+</sup>



**Fig. S2** Energy level splitting of the Mn<sup>4+</sup> ions

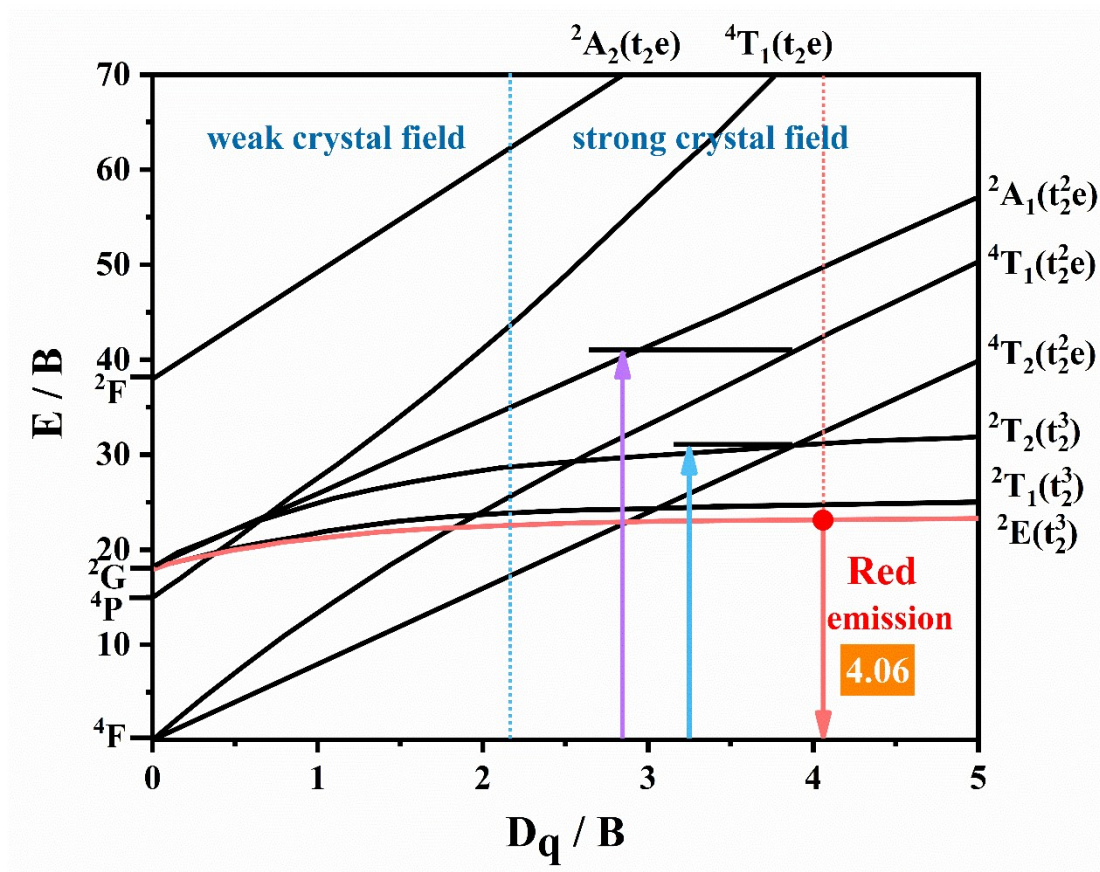
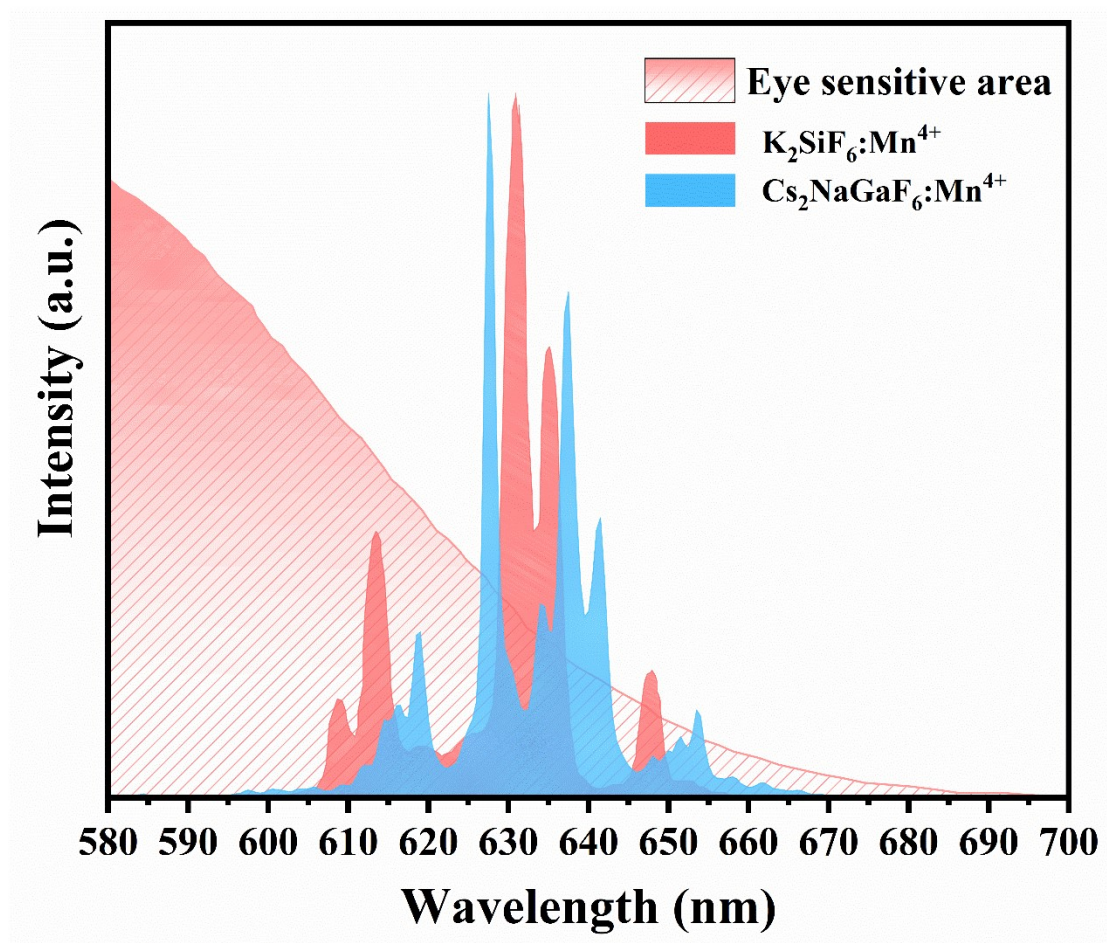


Fig. S3 Tanabe–Sugano diagram of  $\text{Cs}_2\text{NaGaF}_6:\text{Mn}^{4+}$



**Fig. S4** Comparison of matching degree between KSFM and CNGFM and sensitive areas of human eyes

**Table S1.** Refined structural parameters of  $\text{Cs}_2\text{NaGaF}_6:3\%\text{Mn}^{4+}$  sample

Atom	x	y	z	Occ.	Uiso ( $\text{\AA}^2$ )	site
Cs(I)	0	0	0.1277(14)	1	0.0292(26)	6c
Cs(II)	0	0	0.2822(12)	1	0.0262(24)	6c
Na	0	0	0.3924(8)	1	0.0576(30)	6c
Ga(I)	0	0	0	0.985	0.0016(5)	3a
Ga(II)	0	0	0.5000	0.984	0.0139(6)	3b
F(I)	0.1397(13)	-0.1397(13)	0.4584(5)	1	0.0179(13)	18h
F(II)	0.1993(17)	-0.1993(17)	0.6284(4)	1	0.0220(7)	18h
Mn(I)	0	0	0	0.014	0.0065	3a
Mn(II)	0	0	0.5000	0.016	0.0100	3b

**Table S2.** Rietveld refinement results of Cs<sub>2</sub>NaGaF<sub>6</sub>:Mn<sup>4+</sup> and Cs<sub>2</sub>NaGaF<sub>6</sub>.

Formula	Cs <sub>2</sub> NaGaF <sub>6</sub> :3%Mn <sup>4+</sup>	Cs <sub>2</sub> NaGaF <sub>6</sub>
Crystal system	Trigonal	Trigonal
Space group	<i>R-3m</i>	<i>R-3m</i>
a, Å	6.24052(8)	6.24029(7)
b, Å	6.24052(8)	6.24029(7)
c, Å	30.26000(7)	30.25880(7)
α=β(°)	90	90
γ(°)	120	120
V <sub>cell</sub> (Å <sup>3</sup> )	1020.450(29)	1020.5661(27)
Z	6	6
R <sub>WP</sub>	7.08%	6.94%
R <sub>P</sub>	5.51%	5.38%
χ <sup>2</sup>	1.574	1.513

**Table S3.** Vibronic modes and frequencies (cm<sup>-1</sup>) in Cs<sub>2</sub>NaGaF<sub>6</sub>:Mn<sup>4+</sup> crystal.

Mode	Cs <sub>2</sub> NaGaF <sub>6</sub> (ref.24)	Cs <sub>2</sub> NaGaF <sub>6</sub> :Mn <sup>4+</sup> (This work)
TL <sup>1</sup>	56	61
RL <sup>2</sup>	133	139
v <sub>6</sub> <sup>+</sup>	237	238
v <sub>6</sub> <sup>-</sup>	223	212
v <sub>5</sub> <sup>+</sup>	277	-
v <sub>5</sub> <sup>-</sup>	268	-
v <sub>4</sub> <sup>+</sup>	359	335
v <sub>3</sub> <sup>+</sup>	-	646
v <sub>3</sub> <sup>-</sup>	-	588
v <sub>2</sub>	519	-
v <sub>1</sub>	533	-

<sup>1</sup>TL denotes translatory lattice mode.

<sup>2</sup>RL denotes rotatory lattice mode.

**Table S4** Luminous properties of WLEDs and color gamut after filtration

Green	Red	CCT(K)	LE(lm/W)	CIE(x, y)	NTSC(%)	Ref.
					75.0	39
					105.0	39
$\beta$ -SiALON	CaAlSiN <sub>3</sub> :Eu <sup>2+</sup>	8620	38	(0.2883, 02.996)	82.1	9
$\beta$ -SiALON	K <sub>2</sub> NaScF <sub>6</sub> :Mn <sup>4+</sup>	8841	73.7	(0.2852, 0.3159)	105.6	43
$\beta$ -SiALON	Cs <sub>2</sub> MoO <sub>2</sub> F <sub>4</sub> :Mn <sup>4+</sup>	7896	114.7	(0.2948, 0.3104)	109.1	39
$\beta$ -SiALON	Rb <sub>2</sub> NaScF <sub>6</sub> :Mn <sup>4+</sup>	8458	80.7	(0.2891, 0.3056)	108.4	43
$\beta$ -SiALON	Cs <sub>2</sub> NaScF <sub>6</sub> :Mn <sup>4+</sup>	8470	77.0	(0.2852, 0.3159)	105.6	43
$\beta$ -SiALON	Cs <sub>2</sub> NaGaF <sub>6</sub> :Mn <sup>4+</sup>	8302	81.66	(0.3149,0.3262)	118.4%	This work