Supporting Information

Defect-related luminescence behavior of a Mn^{4+} non-equivalently doped fluoroantimonate red phosphor

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Figures

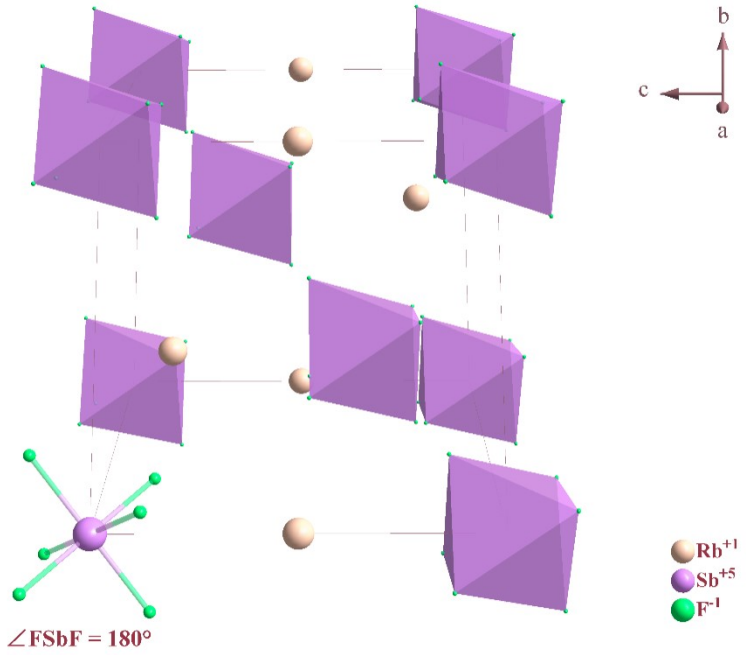


Fig. S1 The unit cell structure of $RbSbF_6$.

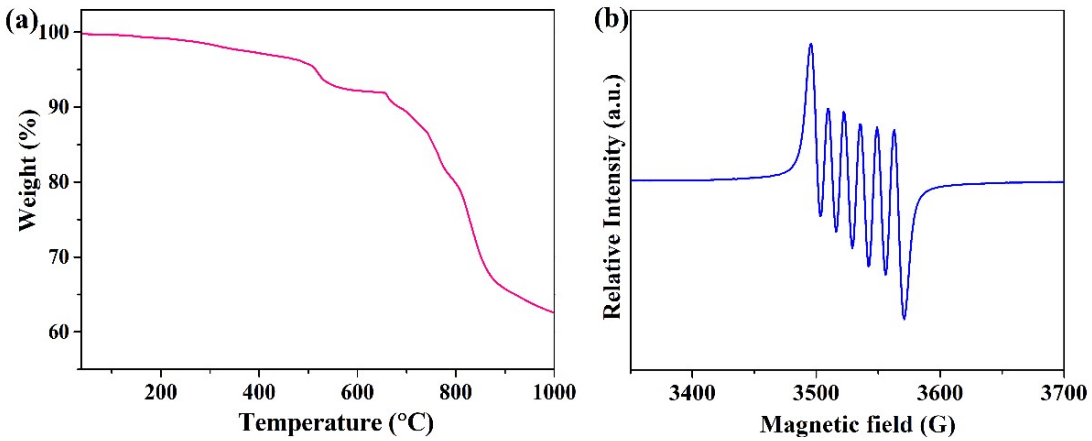


Fig. S2 (a) The TG thermal analysis of $RbSbF_6$ matrix. (b) The EPR spectrum of phosphor $RbSbF_6$:Mn^{4+}.

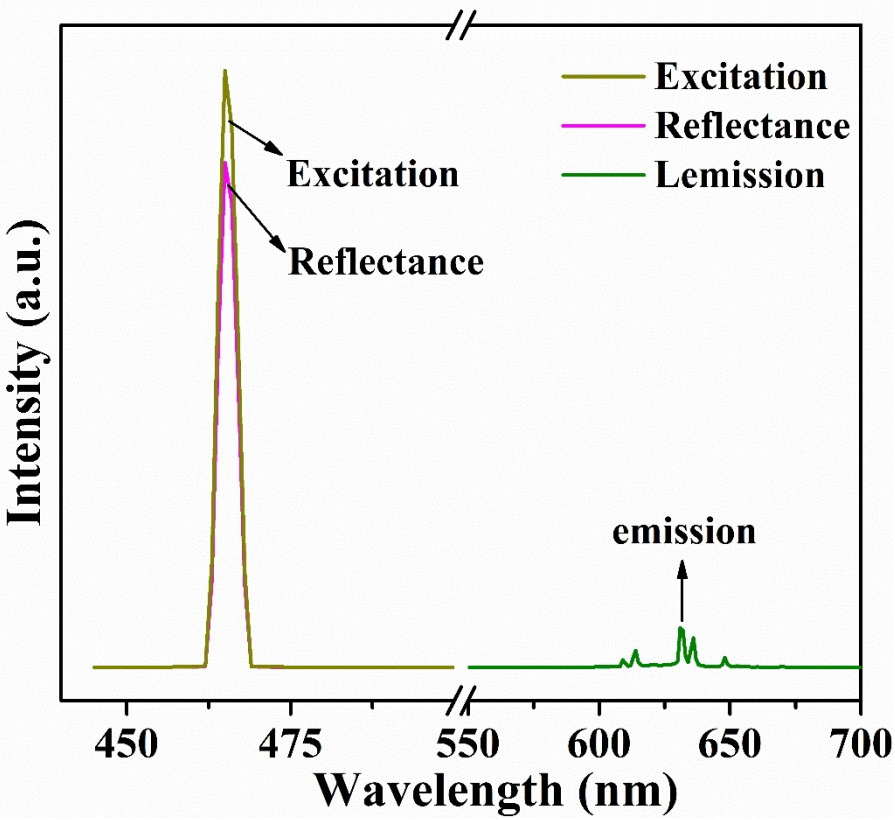


Fig. S3 Excitation of $BaSO_4$ and reflection, emission spectra of $RbSbF_6:Mn^{4+}$ (0.11 %).

The absorption efficiency (AE), IQE, and EQE were calculated definitely by the following equations: [1]

$$AE = \frac{\int \lambda \{E(\lambda) - R(\lambda)\} d\lambda}{\int \lambda \cdot E(\lambda) d\lambda}$$

$$IQE = \frac{\int \lambda \cdot P(\lambda) d\lambda}{\int \lambda \{E(\lambda) - R(\lambda)\} d\lambda} \quad (1)$$

$$EQE = IQE \times AE = \frac{\int \lambda \cdot P(\lambda) d\lambda}{\int \lambda \cdot E(\lambda) d\lambda} \quad (2)$$

where $E(\lambda)/h\nu$, $R(\lambda)/h\nu$, and $P(\lambda)/h\nu$ are the number of photons in the spectra of excitation, reflectance, and emission of phosphor, respectively.

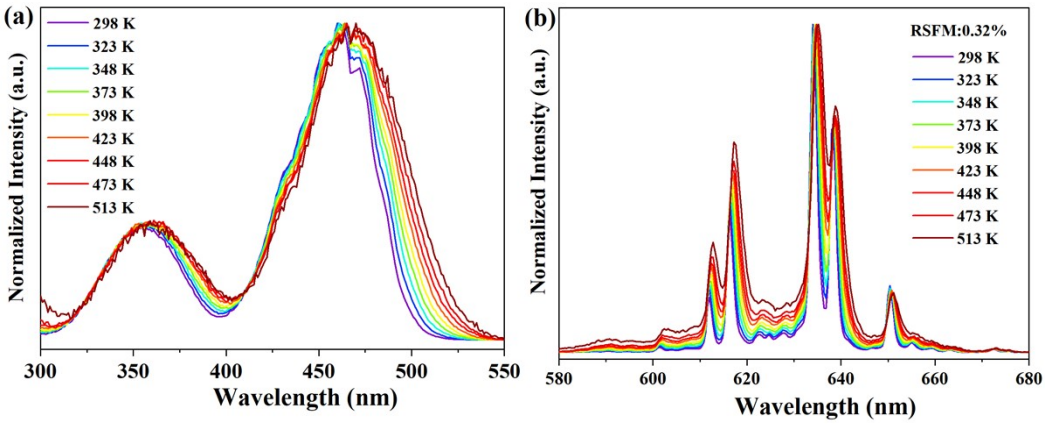


Fig. S4 The normalized (a) PLE and (b) PL of phosphor $RbSbF_6$:0.11%Mn^{4+} as a function of temperature.

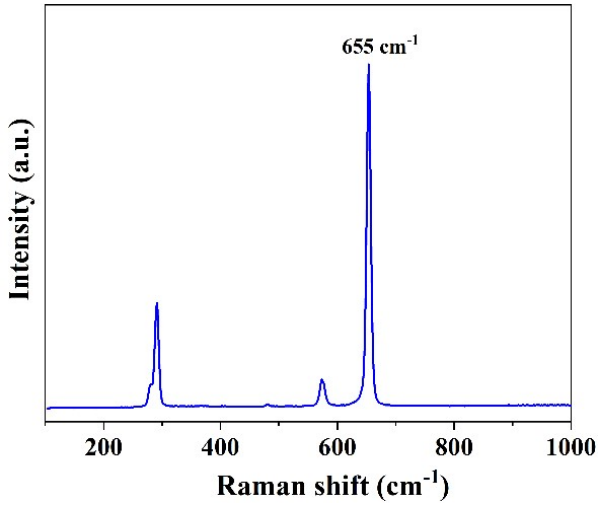


Fig. S5 The Raman spectrum of $RbSbF_6$.

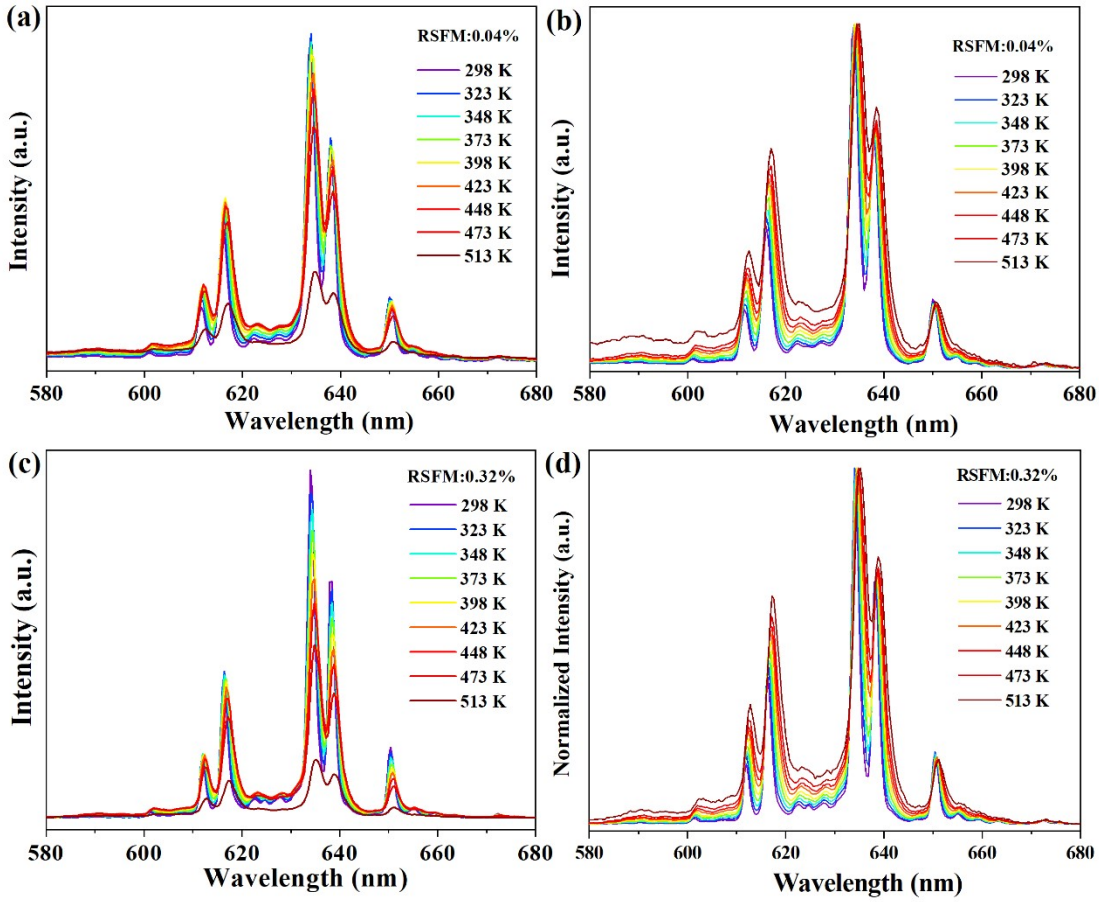


Fig. S6 The temperature-dependent PL and normalized PL of (a, b) RSbFM:0.04% and (c, d) RSbFM:0.32%.

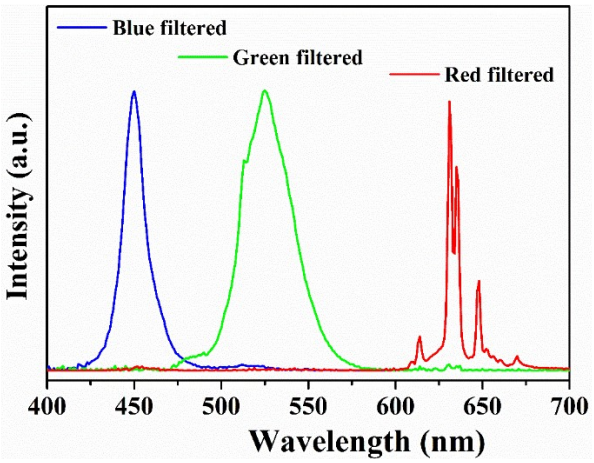


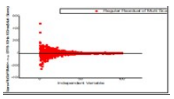
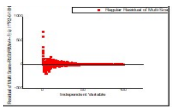
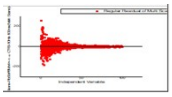
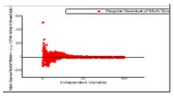
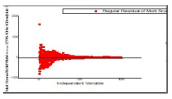
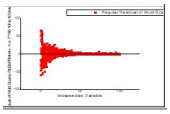
Fig. S7 The emission spectra through commercial blue, green, and red color filters of fabricated WLED using commercial green β-Sialon:Eu^{2+}, blue chip InGaN and $RbSbF_6$:Mn^{4+}.

Tables:

Table S1. ICP results of Mn concentration of $RbSbF_6:Mn^{4+}$ phosphors.

Theoretical concentration (mol %) K_2MnF_6: $RbSbF_6$	Effective concentration (mol %) $RbSbF_6:Mn^{4+}$
0.5	0.04
1.0	0.11
2.0	0.32
5.0	1.29
8.0	4.07
10.0	5.12

Table S2. The lifetime of samples $RbSbF_6:Mn^{4+}$ fitted by single or double exponential function.

Sample (x mol%)	Time counts (ms)		Relative amplitude		Average lifetime (ms)	R^2	Residuals
	$\tau_{radiative}$	$\tau_{non\text{-}radiative}$	$A_{radiative}$	$A_{non\text{-}radiative}$			
0.04	5.7771	--	--	--	5.78	0.9994	
0.11	5.6468	--	--	--	5.65	0.9991	
0.32	5.5726	0.2907	6053.4497	1409.3898	5.51	0.9995	
1.29	5.1339	0.3729	4203.8727	2737.0537	4.92	0.9989	
4.07	4.9644	0.2763	845.5088	3713.8693	4.04	0.9968	
5.12	4.7667	0.2362	435.1032	4603.0734	3.21	0.9959	

The double exponential function is expressed as follows:

$$I(t)=A_1 exp(-\tau/\tau_1)+A_2 exp(-\tau/\tau_2) \quad (1)$$

where I is the luminescence intensity, τ_1 and τ_2 are lifetime components of Mn^{4+} emission, A_1 and A_2 are the weight of these two-lifetime components. The lifetime of Mn^{4+} can be calculated by:

$$\tau=\frac{A_1\tau_1^2+A_2\tau_2^2}{A_1\tau_1+A_2\tau_2} \quad (2).$$

Table R3 The lifetime of some Mn^{4+} non-equivalently or non-octahedrally doped fluorides.

Phosphor	Doping concentration	Lifetime (ms)	*Ref.*
$Na_3AlF_6:Mn^{4+}$	0.6%	5.91	2
$Na_3GaF_6:Mn^{4+}$	0.3%	4.97	3
$KTeF_5:Mn^{4+}$	0.13%	5.41	4
$K_3ZrF_7:Mn^{4+}$	1.73%	4.45	5
$RbSbF_6:Mn^{4+}$	0.11%	5.65	this work

Table S4. Photoelectric parameters of W-LEDs fabricated with blue chips InGaN, commercial green phosphor β-Sialon:Eu^{2+}, and various fluoride red phosphors.

Phosphor	CCT (K)	Efficacy (lm/W)	Chromaticity coordinates (x, y)	NTSC (%)	*Ref.*
$K_2SiF_6:Mn^{4+}$	8000	94	--	85.9	1
$K_3SiF_7:Mn^{4+}$	5686	--	(0.343, 0.341)	81	6
$K_2GeF_6:Mn^{4+}$	5013	103.12	--	120.1	7
$Cs_2SiF_6:Mn^{4+}$	6880	133	(0.302, 0.349)	84.7	8
$Cs_2MnF_6:Si^{4+}$	7856	26.0	(0.2976, 0.3032)	122.3	9
$K_2NaScF_6:Mn^{4+}$	5986	67.65	(0.3219, 0.3356)	127.3	10
$K_2NaScF_6:Mn^{4+}$	8841	73.7	(0.2883, 0.2996)	105.6	11
$Rb_2NaScF_6:Mn^{4+}$	8458	80.7	(0.2891, 0.3056)	108.4	11
$Cs_2NaScF_6:Mn^{4+}$	8470	77.0	(0.2852, 0.3159)	105.6	11
$Cs_2KGaF_6:Mn^{4+}$	--	106.30	(0.2811, 0.3107)	114.6	12
$(NH_4)_3SiF_7:Mn^{4+}$	6844	39.3	(0.3099, 0.3112)	122.8	13
$K_2NbF_7:Mn^{4+}$	4775	78.14	(0.3506, 0.3476)	86.7	14
$KNaMo_2F_4:Mn^{4+}$	4476	81.43	(0.3374, 0.335)	105	15
$K_3HF_2NbOF_5:Mn^{4+}$	6688	95.78	(0.3126, 0.3093)	108.6	16
$RbSbF_6:Mn^{4+}$	10742	103.7	(0.2991, 0.3020)	121.7	this work

Equation

The formation energy of $RbSbF_6:Mn^{4+}$ with one Mn atom substitution on one Sb site of the 2 × 2 × 2 supercell was calculated by DFT using the following equation:

$$E_f = E(doped) - E(pure) - \mu_{Sb} + \mu_{Mn}$$

where E(doped) and E(pure) are the total energies of Sb^{3+} doped system and perfect system, and the u_{Sb} and u_{Mn} are denoted as the chemical potentials of Sb and Mn atoms, respectively. For the metal cations, the chemical potentials were obtained from the calculations of the respective bulk materials. For the F atom, its chemical potential was gained from the calculation of F_2 molecule.

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