Limited Energy Migration and Circumscribed Multiphonon Relaxation Produced Non-Concentration Quenching in a Novel Dazzling Red-Emitting Phosphor

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1. Experimental Section

1.1 Materials and Synthesis

The series of SYWO: xEu^{3+} ($0.1 \leq x \leq 1.0$) samples were prepared by high temperature sintering method. The mixed $SrCO_3$ (99.9%), Y_2O_3 (99.9%), WO_3 (99.9%) and Eu_2O_3 (99.99%) were weighted by stoichiometric ratio and adequately grinding with ethyl alcohol. The mixtures were then shifted to the BN crucible and pre-sintered at 900 ℃ for 4 h. Then the obtained powders were fired at 1400 ℃ for 6 h in N_2 atmosphere. Finally, the as-prepared samples were used for subsequent measurements.

1.2 Measurements

DX-2700BH X-ray diffractometer (XRD) was used to identify the phase purity and characterize the crystal structure with 40 kV and 30 mA by Cu-Ka radiation. Scanning electron microscope (SEM) (Hitachi S-4800) with energy dispersive X-ray was utilized to measure the morphology and elemental distribution. The diffuse reflectance spectra were studied by UV-Vis-NIR spectrophotometer (Lambda 750). A FS5-MCS fluorescence spectrophotometer was used for testing the photoluminescence (PL) spectra in terms of temperature. The lifetimes were recorded by FLS-920T fluorescence spectrophotometer with nanosecond light source.

Table S1. Rietveld refinement results of SYWO and SYWO: $1.0Eu^{3+}$ samples.

Formula	$Sr_9Y_2W_4O_{24}$	SYWO: 1.0Eu^{3+}
Crystal system	orthorhombic	orthorhombic
Space group	*Pmmm* (47)	*Pmmm* (47)
Cell parameters	a = 11.6337 Å, b = 11.5654 Å	a = 11.6641 Å, b = 11.6174 Å
	c =16.4782 Å	c =16.5243 Å
	$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma = 90°$
	V=2217.1154 Å^3	V=2239.1503 Å^3
	Z=4	Z=4
Reliability factors	R_{wp} = 9.70%, R_p = 7.19%,	R_{wp} = 12.58%, R_p = 10.82%,
	χ^2 = 1.69	χ^2 = 2.11

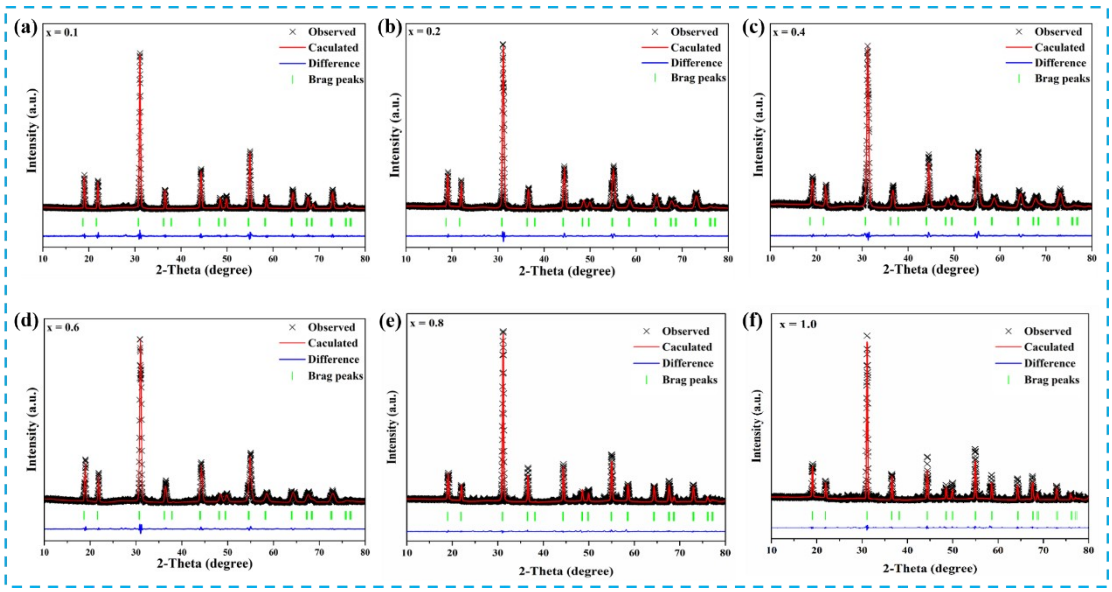

Figure S1. Rietveld refinement of SYWO: xEu^{3+} samples: (a) x = 0.1, (b) x = 0.2, (c) x = 0.4, (d) x = 0.6, (e) x = 0.8, and (f) x = 1.0.

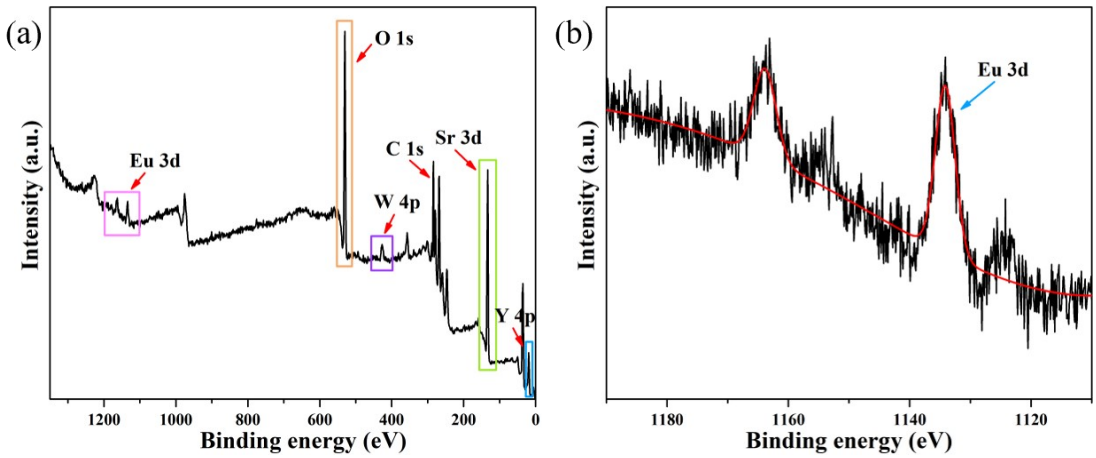

Figure S2 (a) XPS and (b) HR XPS spectra of the representative SYWO: 0.8Eu^{3+} phosphor.

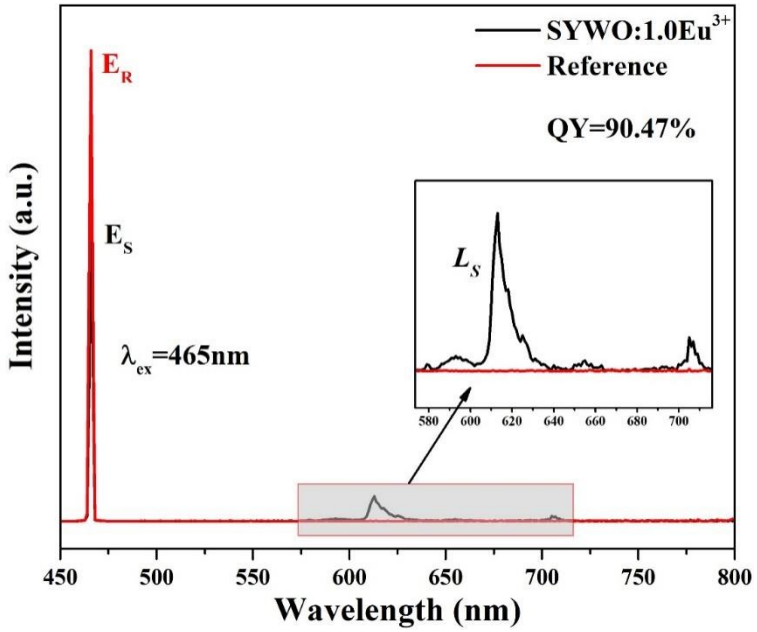

Figure S3. The excitation line of $BaSO_4$ reference and the emission spectrum of SYWO: 1.0Eu^{3+} phosphors excited at 465 nm.

External (η_e) and internal (η_i) quantum efficiencies (QEs) were calculated by using the following equations: [1]

$$\eta_i = \frac{\varepsilon}{\alpha} = \frac{\int L_S}{\int E_R - \int E_S}$$

$$\eta_e = \frac{\varepsilon}{\alpha} = \frac{\int L_S}{\int E_R}$$

where ε is the number of photons emitted by the sample and α is the number of photons absorbed by the sample. L_S is the luminescence emission spectrum of the sample; E_R is the spectrum of the excitation light with $BaSO_4$ in the sphere; E_S is the spectrum of the excitation light with the sample

in the sphere; and all the spectra were collected using the sphere.

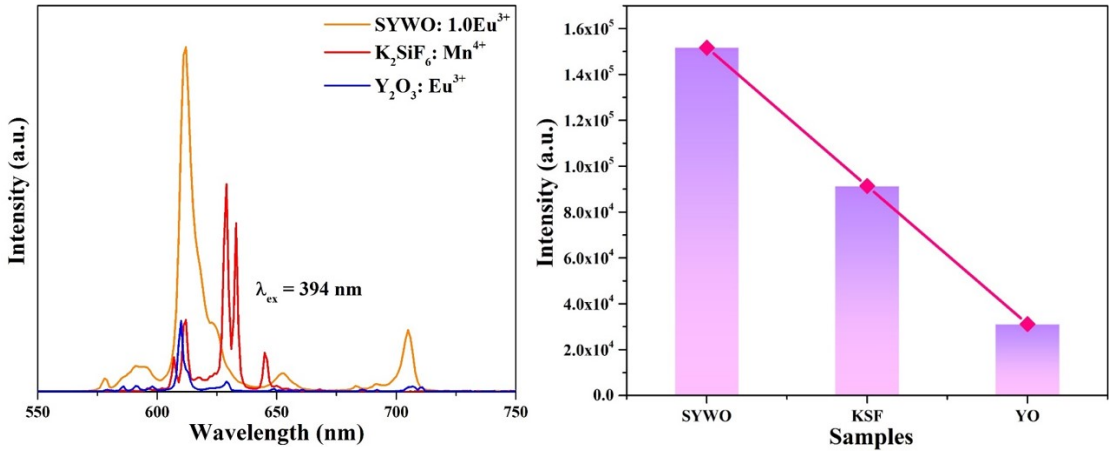

Figure S4. PL intensity of SYWO: 1.0Eu^{3+}, K_2SiF_6: Mn^{4+} and Y_2O_3: Eu^{3+} excited at 394 nm.

Table S2. CIE coordinates, IQE and color purity of SYWO: xEu^{3+} ($0.1 \leq x \leq 1.0$) samples under 465 nm blue light excitation.

Samples (x)	CIE x	CIE y	IQE	EQE	Color purity (%)
0.1	0.6461	0.3526	-	-	94.11
0.2	0.6561	0.3432	-	-	96.64
0.4	0.6567	0.3428	-	-	96.80
0.6	0.6608	0.3389	-	-	97.08
0.8	0.6615	0.3382	-	-	97.26
1.0	0.6628	0.3369	0.905	0.423	97.61
Y_2O_3: Eu^{3+}	0.6435	0.3551	0.080	-	91.83
K_2SiF_6: Mn^{4+}	0.6905	0.3093	0.948	0.452	94.63

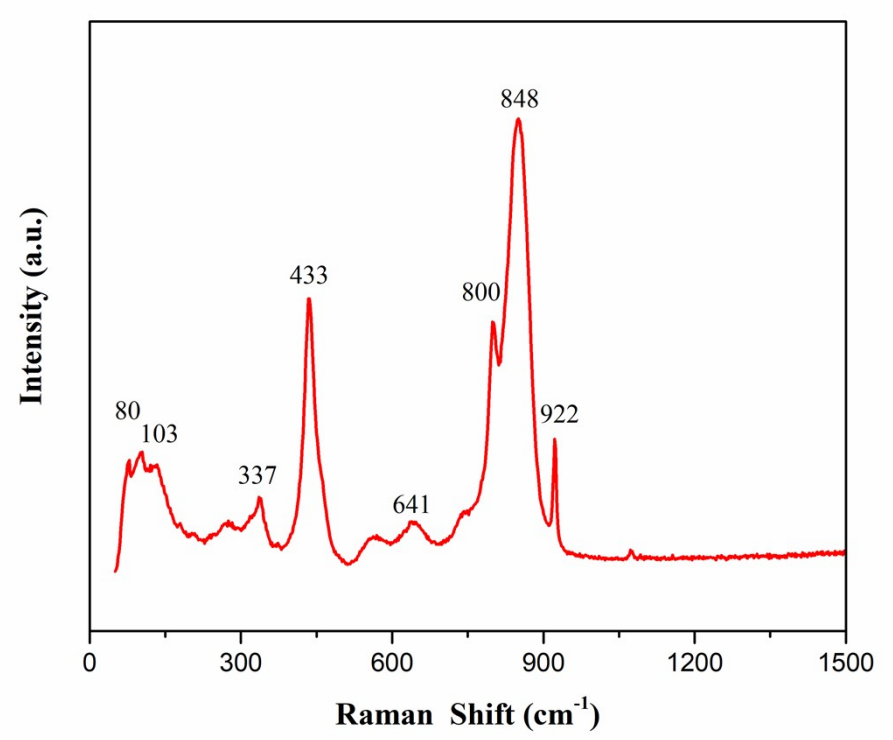

Figure S5. Raman spectrum of SYWO.

Table S3. Comparison of the intensity parameters (Ω2, Ω4) of Eu^{3+} doped different host matrices.

compound	Ω_2	Ω_4	Ω_6	*Ref.*
	(10^{-20} cm^2)	(10^{-20} cm^2)	(10^{-20} cm^2)	
SYWO:Eu^{3+}	13.08	3.91	-	This work
$La_2(MoO_4)_2$:Eu^{3+}	10.7	1.07	0.56	[2]
$NaGdTiO_4$:Eu^{3+}	6.02	1.51	0.37	[3]
$Gd_2(W_{0.5}Mo_{0.5})O_6$:Eu^{3+}	6.91	0.22	-	[4]
BiOCl:Eu^{3+}	2.78	1.72	-	[5]
$Y_{10}W_2O_{11}$:Eu^{3+}	4.20	0.23	-	[6]

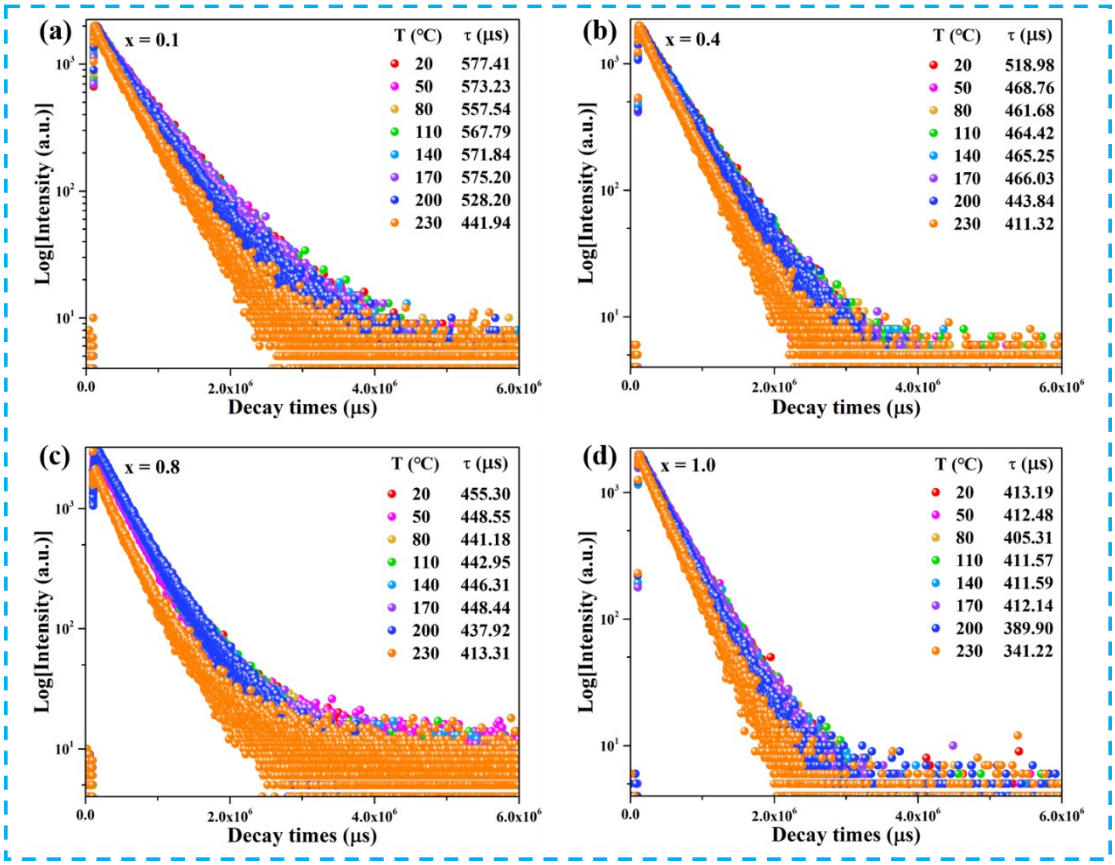

Figure S6. PL decay lifetimes of SYWO: xEu^{3+} samples: (a) x = 0.1, (b) x = 0.4, (c) x = 0.8, and (d) x = 1.0.

Table S4. CIE coordinates and color purity of SYWO: $1.0Eu^{3+}$ at different temperature.

T (°C)	CIE x	CIE y	Color purity (%)
20	0.6598	0.3399	97.61
50	0.6592	0.3405	97.45
80	0.6587	0.341	97.32
110	0.6582	0.3416	97.19
140	0.6602	0.3396	96.93
170	0.6568	0.3429	96.06
200	0.6558	0.3439	96.58
230	0.6543	0.3454	96.19

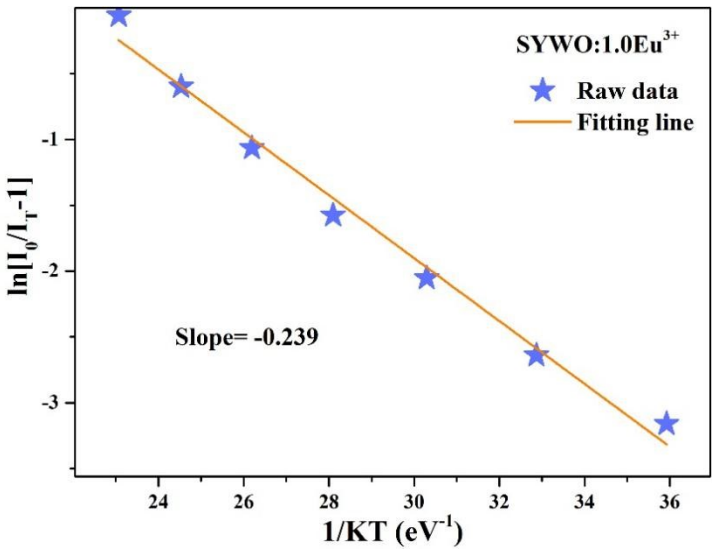

Figure S7. Activation energy of SYWO: 1.0Eu^{3+} phosphor.

Activation energy (E_a) is a key parameter used to measure thermal stability and can be calculated by Arrhenius equation (1): [7]

$$I_T = \frac{I_0}{1 + Aexp\left(-\frac{\Delta E}{kT}\right)} \quad (1)$$

Where I_0 and I_T represent for the emission intensities of the emission spectra at room temperature (20 °*C*) and at a given temperature T (*K*), respectively. *k* represents the Boltzmann constant (8.626 ×10-5 *eV*), *A* represents a constant, and *ΔE* represents the calculated activation energy. [8] The relationship between $\ln[(I_0/I_T) - 1]$ and $1/kT$ of SYWO: 1.0Eu^{3+} is plotted in Figure S7, and the slope of the line is -0.239 by fitting, and the estimated *ΔE* is 0.239 eV.

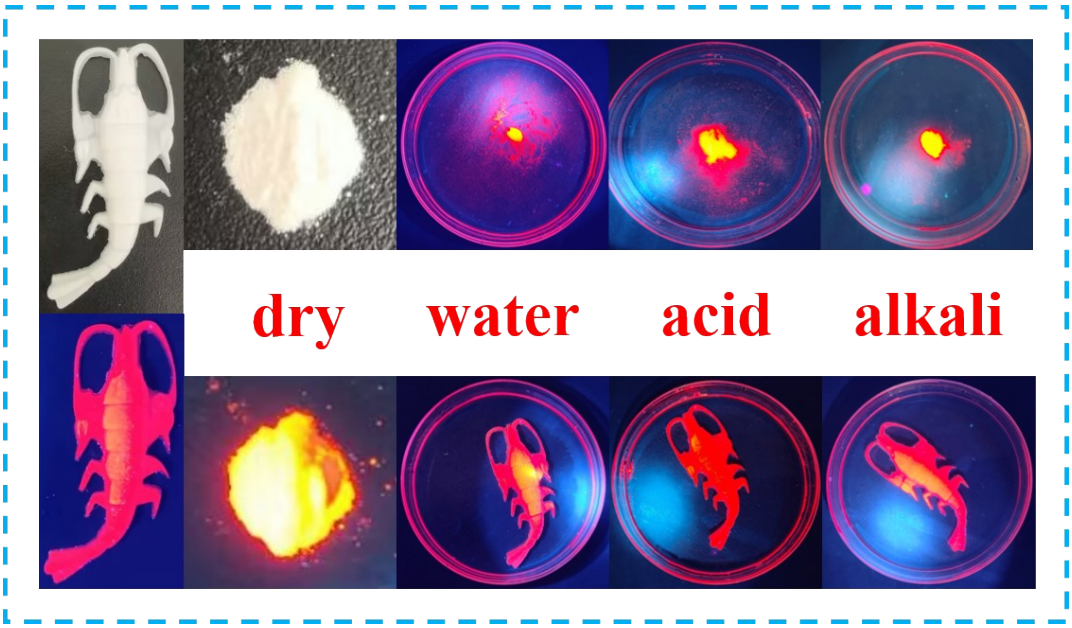

Figure S8. Digital photographs in natural light and 395 nm n-UV LED chip excitation of the 3D artwork in dry and water, acid, alkali solution environment.

Table S5. Comparison of SYWO: 1.0Eu^{3+} phosphor with some reported red-emitting phosphors in quantum efficiency (QE), thermal stability (I_{400K}/I_{300K}) and color purity.

Phosphors	QE	I_{400K}/I_{300K}	Color purity	Ref.
SYWO:Eu^{3+}	90.47%	94.80%	97.61%	This work
$LaSc_3(BO_3)_4$:Eu^{3+}	89.00%	88.00%	94.20%	[9]
$NaBiF_4$:Eu^{3+}	75.90%	73.10%	90.40%	[10]
$Ca_3Y_2B_4O_{12}$:Eu^{3+}	95.60%	76.10%	88.57%	[11]
$NaGdF_4$:Eu^{3+}	62.30%	61.00%	90.50%	[12]
Y_2O_3:Eu^{3+}	83.40%	75.40%	-	[13]
Y_2O_2S:Eu^{3+}	68.68%	79.60%	-	[14, 15]
Ca_2LuTaO_6:Eu^{3+}	74.00%	80.80%	95.80%	[16]
La_3SbO_7:Eu^{3+}	63.80%	84.50%	-	[17]
$Ca_4LaO(BO_3)_3$:Eu^{3+}	98.10%	78.60%	-	[18]
$K_2SrGe_8O_{18}$:Eu^{3+}	57.60%	83.70%	95.50%	[19]
$Na_3Sc_2(PO_4)_3$:Eu^{3+}	49.00%	77.90%	87.00%	[20]
$K_2Tb(PO_4)(WO_4)$:Eu^{3+}	76.40%	93.48%	-	[21]

$K_2TiF_6:Mn^{4+}$	92.20%	100.00%	-	[22]

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