Tunable luminescence via Cr^{3+}-Yb^{3+}/Nd^{3+} energy transfer in Cr^{3+} and Yb^{3+}/Nd^{3+} coactivated NIR phosphors for non-destructive analysis

Xiaowei Zhang[a,b], Dashuai Sun[b], Pengcheng Luo[b], Luhui Zhou[b], Xinyu Ye[a]*, Hongpeng You[b]*

a College of Rare Earths, Jiangxi University of Science and Technology, Ganzhou, Jiangxi 341000, P. R. China

b Key Laboratory of Rare Earths, Chinese Academy of Sciences; Ganjiang Innovation Academy, Chinese Academy of Sciences, Ganzhou 341000, P. R. China

E-mail: xinyye@yahoo.com; hpyou@ciac.ac.cn

Table S1 Refined structural parameters and cell parameter values of $Y_3ScAl_4O_{12}$:0.10Cr^{3+} from Rietveld refinement.

Formula			$Y_3ScAl_4O_{12}$		
Crystal system			cubic		
Space group			$Ia3\,d$		
Cell parameters			a = b = c = 12.189 Å		
			Alpha = Beta = Gamma = 90°		
Cell volume			1793.167 $Å^3$		
Reliability			R_p = 4.725%		
factors			R_{wp} = 7.05%		
			χ^2 = 1.4785		
Atom	x	y	z	Uiso / $Å^2$	occupancy
Al1	0.000	0.000	0.000	0.00102	0.8
Al2	0.375	0.000	0.250	0.00266	0.8
Sc1	0.000	0.000	0.000	0.00102	0.2
Sc2	0.375	0.000	0.250	0.00266	0.2
Y1	0.125	0.000	0.250	0.00368	1
O1	-0.039396	0.054699	0.157297	0.00132	1

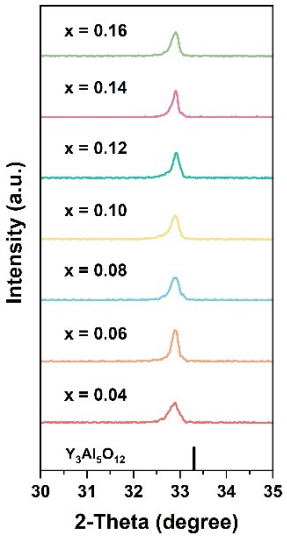

Figure S1 The magnification XRD image.

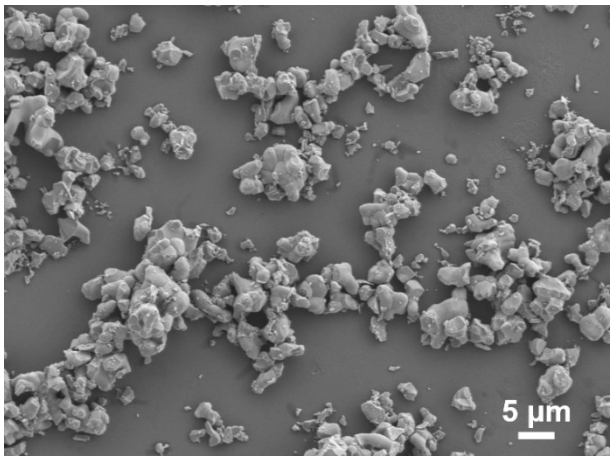

Figure S2 The SEM imaging of YSAO:0.10Cr^{3+}.

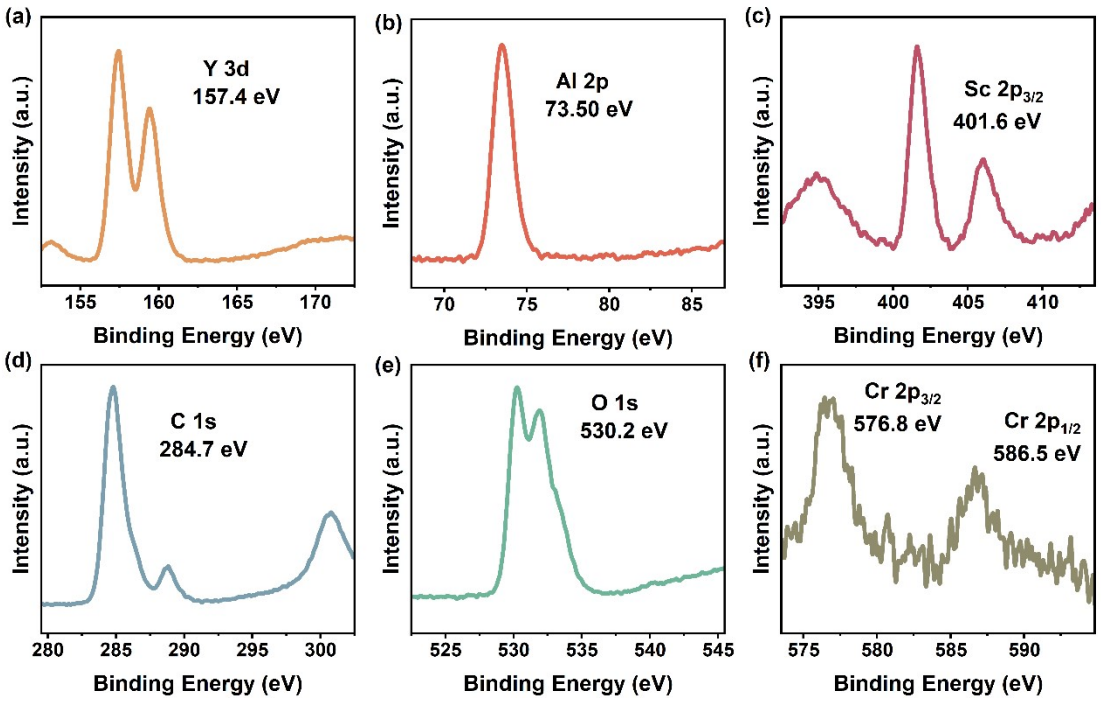

Figure S3 The corresponding deconvoluted peaks in the high-resolution spectra for Y-3d, Al-2p, Sc-2p, C-1s, O-1 s, and Cr-2p elements.

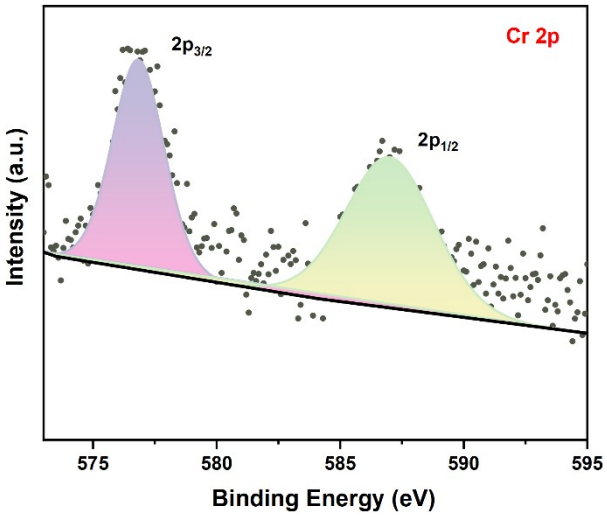

Figure S4 Cr 2p XPS spectrum of the YSAO:0.10Cr^{3+}.

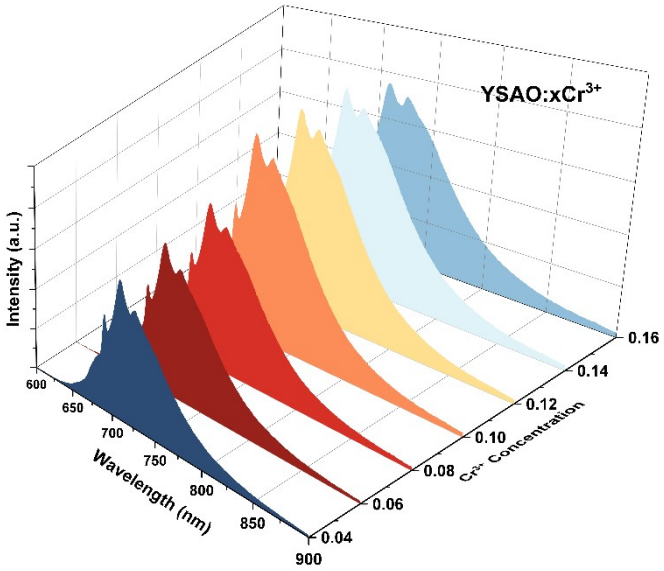

Figure S5 PL spectra of YSAO: xCr^{3+} (x = 0.04-0.16) for different Cr^{3+} concentrations.

Supporting Note S1:

The following equation can be used to calculate the critical distance for energy transfer which helps understand the mechanism of concentration quenching of Cr^{3+} in YSAO[1]:

$$R_c = 2(\frac{3V}{4\pi x_c N})^{1/3} \quad (1)$$

Where, x_c is the critical concentration value of doping ions in the matrix, V is the cell volume of the matrix, and N is the number of atoms contained in the unit cell. It is known that the cell volume $V = 1793.167$ Å, $N = 16$. and $x_c = 0.10$. The calculated values are $R_c = 13.30$ Å. It is suggested that the concentration quenching of Cr^{3+} in YSAO is not due to the exchange interaction, but may be caused by the electric multipole interaction.

According to the energy transfer theory of Dexter and Uitert, when the doping amounts of activated ions is large, there is a relationship between the emission intensity and the mole fraction of activated ions[2]:

$$Log(\frac{I}{x}) = -\frac{\theta}{3} Logx + A \quad (2)$$

Where I represents the emission intensity, *I* represent the emission intensity corresponding to the ion concentration, *x* represents the ion concentration. As shown in Figure S4, the relation between Log I/x and Log x can be fitted as a line by processing formula (2). The relationship between Log I/x and Log x is line with a slope of 1.38 ($-\theta/3 = -1.38$). Therefore, the calculated θ is 4.14, which θ is approximately equal to 6. The result reveals that the main concentration quenching mechanism of Cr^{3+} in YSAO is the dipole-dipole interaction.

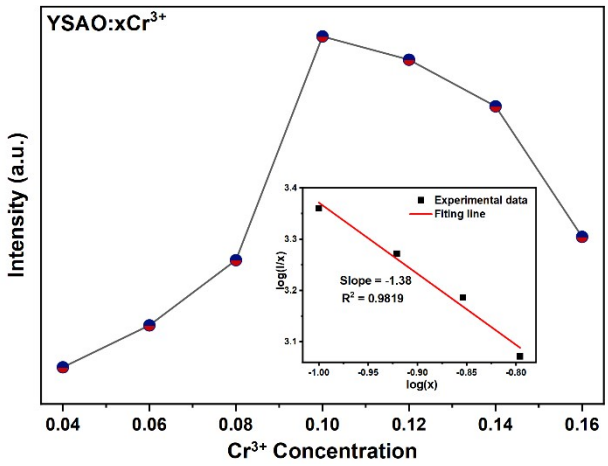

Figure S6 Linear relationship between Log(x) and Log(I/x).

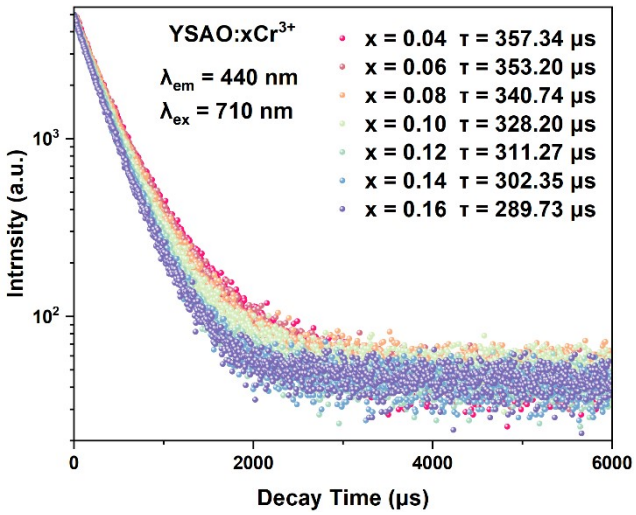

Figure S7 Luminescence decay curves of YSAO:xCr^{3+} ($0.04 \leq x \leq 0.16$) phosphors.

Supporting Note S2:

The activation energy can be calculated using the following equation[3]:

$$I(T) = \frac{I_0}{1 + A\exp(-\frac{\Delta E}{kT})} \quad (3)$$

where I_0 is the initial emission intensity, $I_{(T)}$ is the intensity at a given temperature T, k is the Boltzmann constant (8.617×10^{-5} eV K^{-1}), A is a constant, and ΔE is the activation energy leading to thermal quenching. The relationship between ln ($I_0/I_{(T)}$ - 1) and 1/kT is shown in Figure S5. The calculated ΔE value is 0.25 eV.

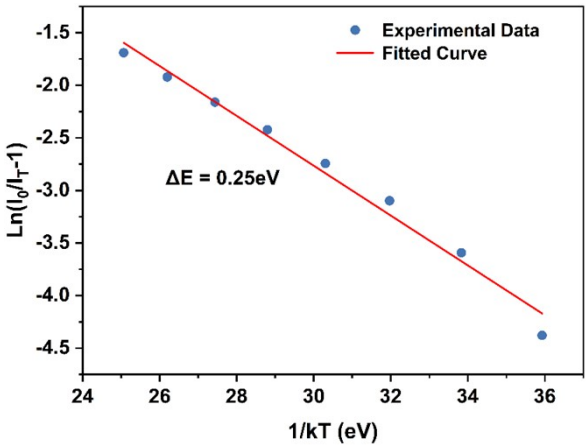

Figure S8 Calculated activation energy fitting curves for YSAO:0.10Cr^{3+}.

Supporting Note S3:

The internal quantum efficiency (IQE) and external quantum efficiency (EQE) of the YSAO:0.10Cr^{3+} phosphor were further determined, and the IQE can be calculated by the following formula[4]:

$$IQE = \frac{\int L_S}{\int E_R - \int E_S} \quad (4)$$

where L_S is the emission spectrum of the sample under study, E_S is the spectrum of the light used to excite the sample, and E_R is the spectrum of the excitation light without the sample in the integrating sphere.

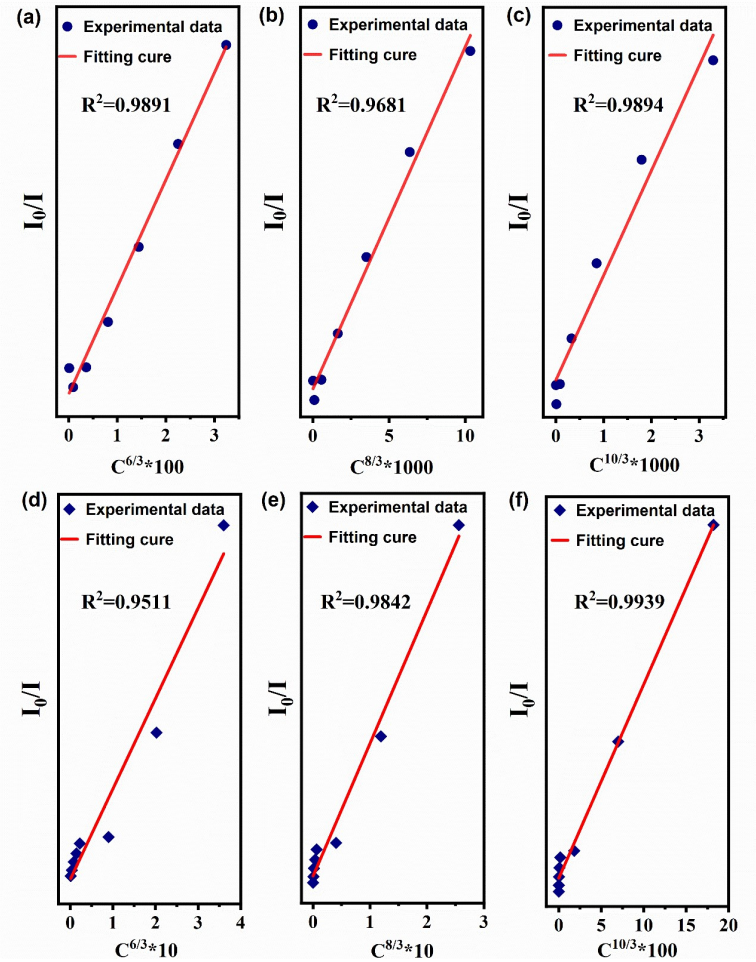

Figure S9 Fitting curves of I_0/I versus $C^{n/3}$ (n = 6, 8, 10).

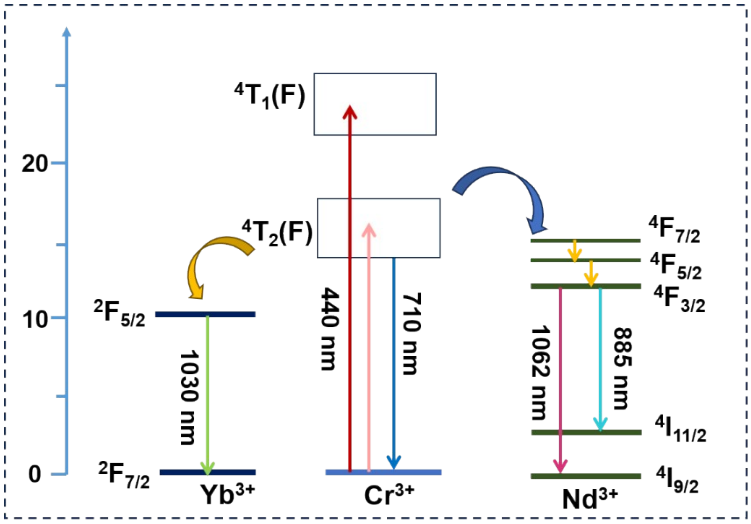

Figure S10 Schematic representation energy transfer.

[1] Z. Lu, D. Sun, Z. Lyu, S. Shen, L. Wang, J. Wang, H. Zhao, H. You, Novel efficient $SrMgY_3(SiO_4)_3F:Ce^{3+}$, Tb^{3+} phosphor with tunable color and thermal stability through energy transfer, Journal of the American Ceramic Society, 106 (2023) 1182-1193.

[2] Z.H. Yue, D.S. Sun, Z. Lyu, S.D. Shen, C. Lyu, P.C. Luo, H.P. You, A highly thermally stable $Y_3AlGa_4O_{12}:Cr^{3+}$ phosphor for near-infrared pc-LEDs, Journal of Materials Chemistry C, 11 (2023) 16563-16570.

[3] L. Jiang, X. Jiang, J. Xie, H. Sun, L. Zhang, X. Liu, Z. Bai, G. Lv, Y. Su, Ultra-broadband near-infrared $Gd_3MgScGa_2SiO_{12}$: Cr, Yb phosphors: Photoluminescence properties and LED applications, Journal of Alloys and Compounds, 920 (2022) 165912.

[4] Y. Jin, Z. Zhou, R. Ran, S. Tan, Y. Liu, J. Zheng, G. Xiang, L. Ma, X.j. Wang, Broadband NIR phosphor $Ca_2LuScAl_2Si_2O_{12}:Cr^{3+}$ for NIR LED applications, Advanced Optical Materials, 10 (2022) 2202049.