Electronic supplementary information

Efficient and stable near-infrared $Y_2Mg_2Al_2Si_2O_{12}:Cr^{3+}$ phosphor: analysis of luminescence source by site elimination strategy

Yixin Sun,[a] Mengmeng Shang,*[a] Yining Wang,[a] Yiying Zhu,[a] Xiaole Xing,[a] Peipei Dang, [b] and Jun Lin*[b]

[a] Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials Ministry of Education, School of Material Science and Engineering, Shandong University, 17923 Jingshi Road, Jinan 250061, P. R. China. E-mail: mmshang@sdu.edu.cn

[b] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China. E-mail: jlin@ciac.ac.cn

Table S1 The calculated average lifetime of YMAS:xCr^{3+} (x = 1% ~ 22%) monitored at the optimal monitoring wavelength by excitation by 430 nm.

Cr^{3+} concentration	τ^* (μs)	A_1	τ_1(μs)	A_2	τ_2(μs)	optimal monitoring wavelength (nm)
1%	163.1	1704	234.42	4468	65.14	715
2%	147.6	1867	209.18	4542	61.18	745
6%	106.5	1961	151.83	4773	49.79	755
10%	80.2	1510	126.22	5596	46.48	770
14%	65.0	574	138.13	6514	45.29	785
18%	53.5	482	120.68	6827	38.70	792
22%	45.8	503	103.76	7339	33.45	810

Table S2 The content of each element in YMA_4S:2%Cr^{3+}.

Element	Original solution element concentration C_1 (mg/L)	Test solution element Concentration C_0 (mg/L)	dilution multiple (f)	element content W (%)
Y	647.469	6.475	100	34.08
Mg	77.914	77.791	10	4.10
Al	327.086	3.271	100	17.22
Si	102.700	1.027	100	5.30
Cr	2.9122	2.912	1.0	0.15

Table S3 Main parameters of processing and refinement results of $Y_2Mg_{2-y}Al_{2+2y}Si_{2-y}O_{12}$:2%$Cr^{3+}$ (y = 0 and 1).

Compound	y = 0	y = 1
$a = b = c$, Å	11.9667(8)	11.9530(11)
V, Å^3	1713.69	1707.78
$\alpha = \beta = \gamma$, °	90	90
R_{wp}, %	8.96	9.53
R_p, %	7.52	8.72
χ^2	3.27	3.09

Table S4 Final refined atomic coordinates, occupancy and B_{eq} for $Y_2Mg_{2-y}Al_{2+2y}Si_{2-y}O_{12}$:2%$Cr^{3+}$ (y = 0 and 1).

$Y_2Mg_{2-y}Al_{2+2y}Si_{2-y}O_{12}$:2%$Cr^{3+}$ (y = 0)						
Atom	Mult.	x	y	z	Occ.	B_{eq}
Al1	16a	0.000000(0)	0.000000(0)	0.000000(0)	0.4720(2)	0.0181(7)
Mg1	16a	0.000000(0)	0.000000(0)	0.000000(0)	0.5077(2)	0.0181(7)
Cr1	16a	0.000000(0)	0.000000(0)	0.000000(0)	0.0203(2)	0.0181(7)
Al2	24d	0.250000(0)	0.375000(0)	0.000000(0)	0.2876(2)	0.0209(4)
Si1	24d	0.250000(0)	0.375000(0)	0.000000(0)	0.6970(2)	0.0209(4)
Cr2	24d	0.250000(0)	0.375000(0)	0.000000(0)	0.0154(2)	0.0209(4)
Y1	24c	0.250000(0)	0.125000(0)	0.000000(0)	0.7316(2)	0.0097(9)
Mg2	24c	0.250000(0)	0.125000(0)	0.000000(0)	0.2684(2)	0.0097(9)
O1	96h	0.035842(5)	0.054675(7)	0.656871(4)	1.0	0.0276(6)

$Y_2Mg_{2-y}Al_{2+2y}Si_{2-y}O_{12}$:2%$Cr^{3+}$ (y = 1)						
Atom	Mult.	x	y	z	Occ.	B_{eq}
Al1	16a	0.000000(0)	0.000000(0)	0.000000(0)	0.9525(3)	0.0169(3)
Cr1	16a	0.000000(0)	0.000000(0)	0.000000(0)	0.0475(3)	0.0169(3)
Al2	24d	0.250000(0)	0.375000(0)	0.000000(0)	0.6732(4)	0.0254(1)
Si1	24d	0.250000(0)	0.375000(0)	0.000000(0)	0.3136(4)	0.0254(1)
Cr2	24d	0.250000(0)	0.375000(0)	0.000000(0)	0.0132(4)	0.0254(1)
Y1	24c	0.250000(0)	0.125000(0)	0.000000(0)	0.7386(3)	0.0146(3)
Mg2	24c	0.250000(0)	0.125000(0)	0.000000(0)	0.2614(3)	0.0146(3)
O1	96h	0.030509(2)	0.054747(1)	0.651329(4)	1.0	0.0249(1)

Table S5 The calculated average lifetime of $YMA_4S:xCr^{3+}$ (x = 2% ~ 15%) monitored at 771 nm.

Cr^{3+} concentration	τ^* (μs)	A_1	τ_1 (μs)	A_2	τ_2 (μs)
2%	185.1	2052	240.6	3564	63.1
6%	166.6	1915	225.8	3915	63.1
8%	139.5	2250	183	3799	57.4
10%	132.2	1815	188.2	4400	60.9
12%	118.7	1401	183.4	4725	61.8
15%	96.5	1260	157.6	5236.5	33.45

Table S6 The calculated average lifetime of $YMA_4S:xCr^{3+}$ (x = 2% ~ 15%) monitored at 855 nm.

Cr^{3+} concentration	τ^* (μs)	A_1	τ_1 (μs)	A_2	τ_2 (μs)
2%	122.8	1779	171.7	4347	443.1
6%	122.6	1705	176.5	4503	48.9
8%	116.0	1708	169.9	4785	48.1
10%	108.3	1514	166.9	5099	48.7
12%	97.4	1279	160.4	5450	48.4
15%	95.6	1279	160.4	5876	43.45

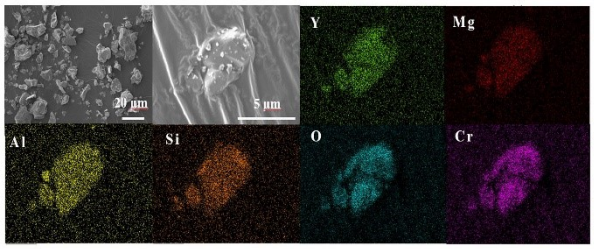

Fig. S1 SEM image and elemental mapping images of YMAS:2%Cr^{3+}.

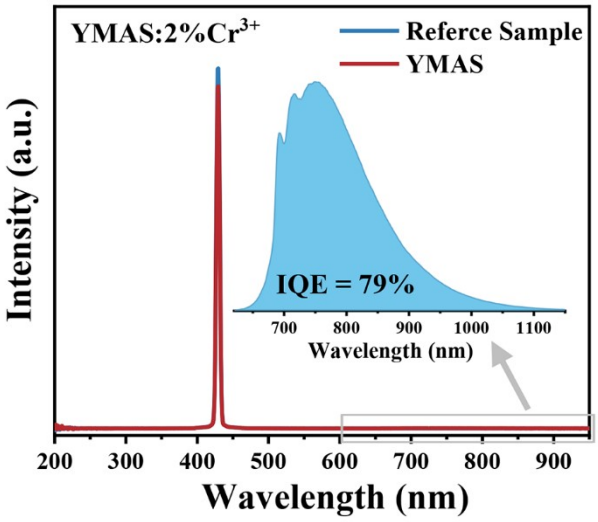

Fig. S2 The quantum yield diagram of YMAS:2%Cr^{3+}.

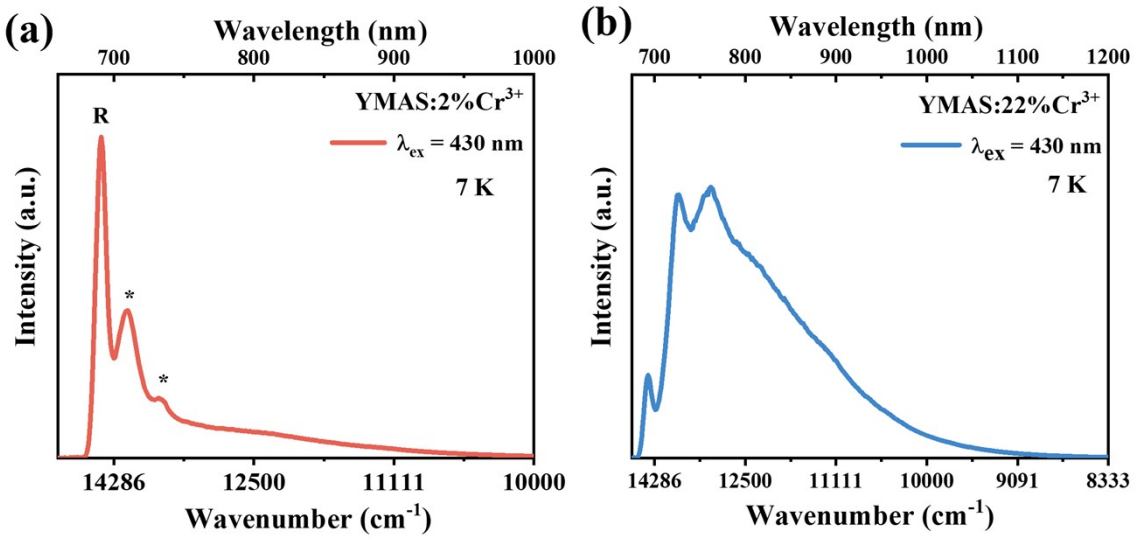

Fig. S3 The PL spectra of (a)YMAS:2%Cr^{3+} and (b) YMAS:22%Cr^{3+} for temperatures at 7 K.

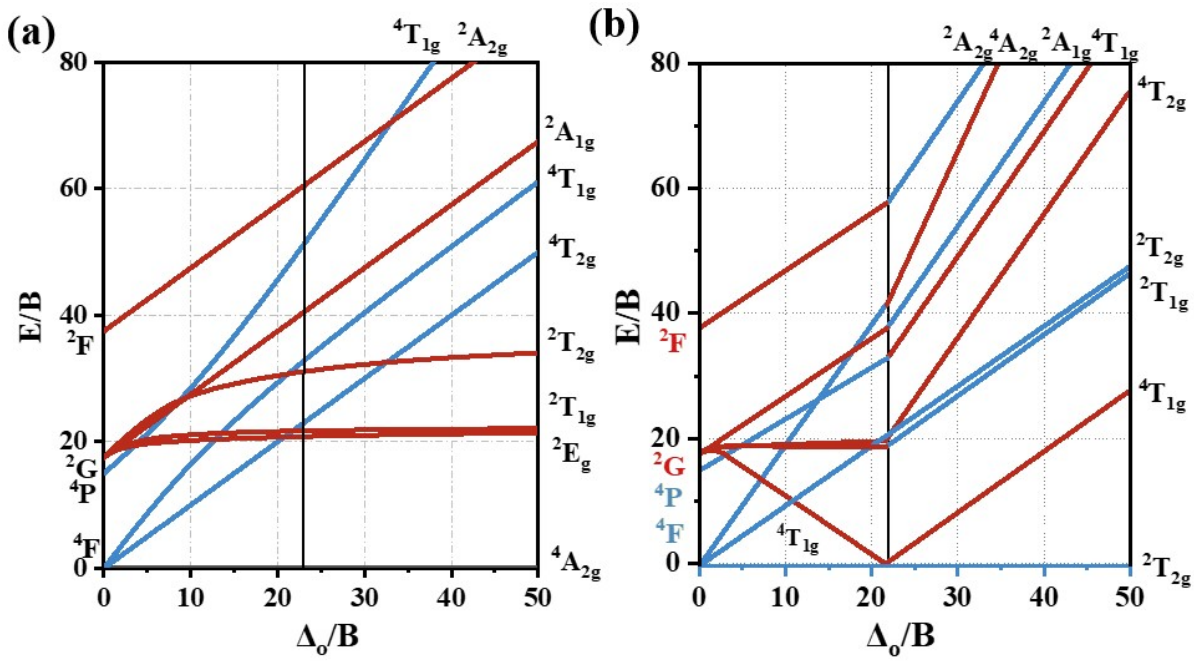

Fig. S4 Tanabe-Sugano diagram for Cr^{3+} ion in (a) octahedral coordination, and (b) tetrahedral coordination.

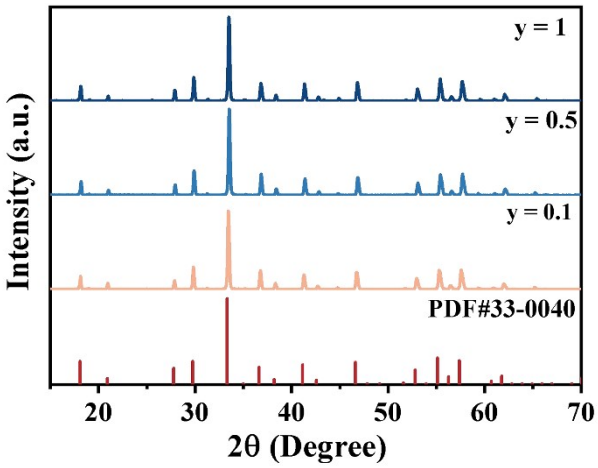

Fig. S5 XRD patterns of the $Y_2Mg_{2-y}Al_{2+2y}Si_{2-y}O_{12}$:2%$Cr^{3+}$(y = 0.1, 0.5 and 1).

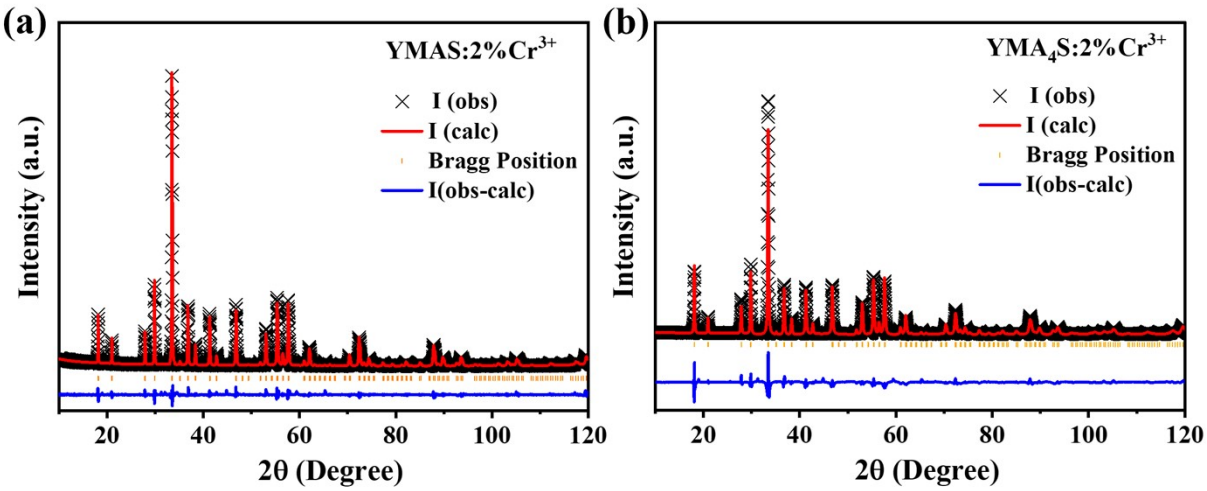

Fig. S6 Rietveld refinement of (a) YMAS:2%Cr^{3+} and (b) YMA_4S:2%Cr^{3+}.

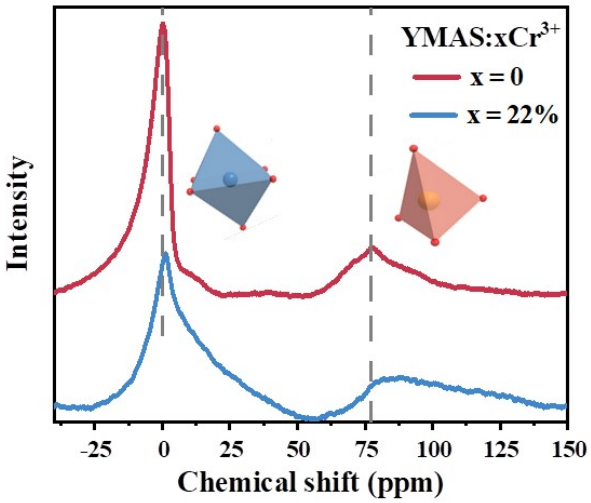

Fig. S7 ^{27}Al ss-NMR spectra of YMAS:xCr^{3+} (x = 0, 22%).

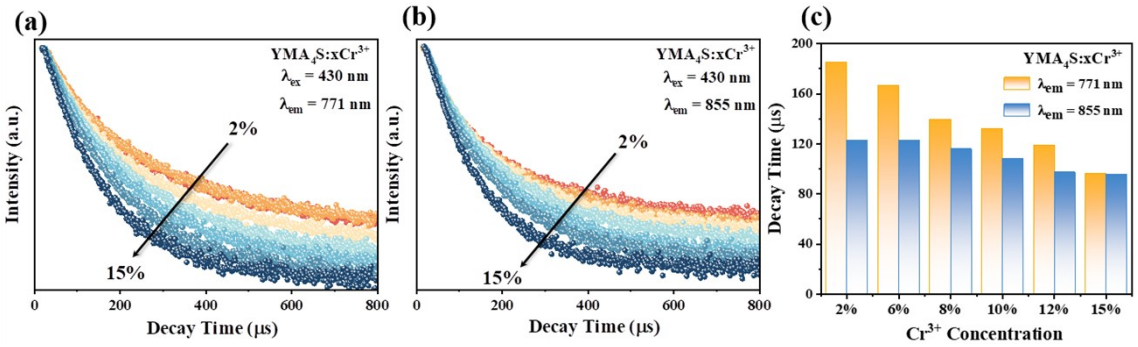

Fig. S8 Fluorescence decay curves of $YMA_4S:xCr^{3+}$ (x = 2% ~ 15%) monitored at (a) 771 and (b) 855 nm. (c) The different decay rates of the Cr1 (771 nm) and Cr2 (855 nm) in $YMA_4S:xCr^{3+}$.

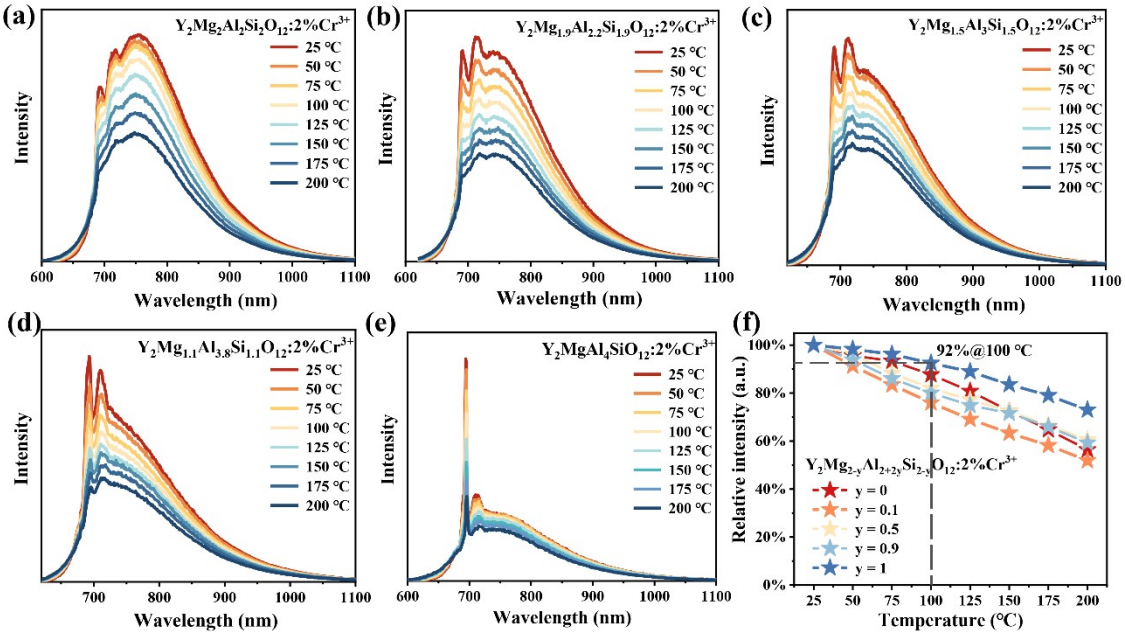

Fig. S9 Temperature - dependent PL spectra of $Y_2Mg_{2-y}Al_{2+2y}Si_{2-y}O_{12}$:2%$Cr^{3+}$ (a) y = 0, (b) y = 0.1, (c) y = 0.5, (d) y = 0.9 and (e) y = 1. (f) Temperature-dependent integral intensity of $Y_2Mg_{2-y}Al_{2+2y}Si_{2-y}O_{12}$:2%$Cr^{3+}$ (y = 0, 0.1, 0.5, 0.9 and 1).

The optical band gap can be calculated using the following Kubelka - Munk formula[S1, S2]:

$$F(R) = \frac{(1-R)^2}{2R} \quad \text{(S1)}$$

$$[F(R) \times hv]^{1/n} = A(hv - E_g) \quad \text{(S2)}$$

where *F(R)* is the absorption, *R* is the reflectance, *hv* is the photon energy, *A* is the absorption constant, and E_g is the optical band gap. The *n* values determined by the directly allowed transition, directly forbidden transition, indirectly allowed transition, and indirectly forbidden transition are 1/2, 3/2, 2, and 3, respectively. The electronic transition of this garnet belongs to directly allowed transition (n = 1/2), so the E_g of YMAS is estimated to be 5.87 eV.

References

[S1] C. Li, J. Zhong, *Chem. Mater.* **2022**, *34*, 8418.

[S2] T. Gao, W. Zhuang, R. Liu, Y. Liu, X. Chen, Y. Xue, *J. Alloys Compd.* **2020**, *848*, 156557.