Supporting Information

A High-efficiency Blue-LED-excitable Broadband Cr^{3+}/Ni^{2+} Co-doped Garnet Phosphor toward Next-generation Spectroscopy Application

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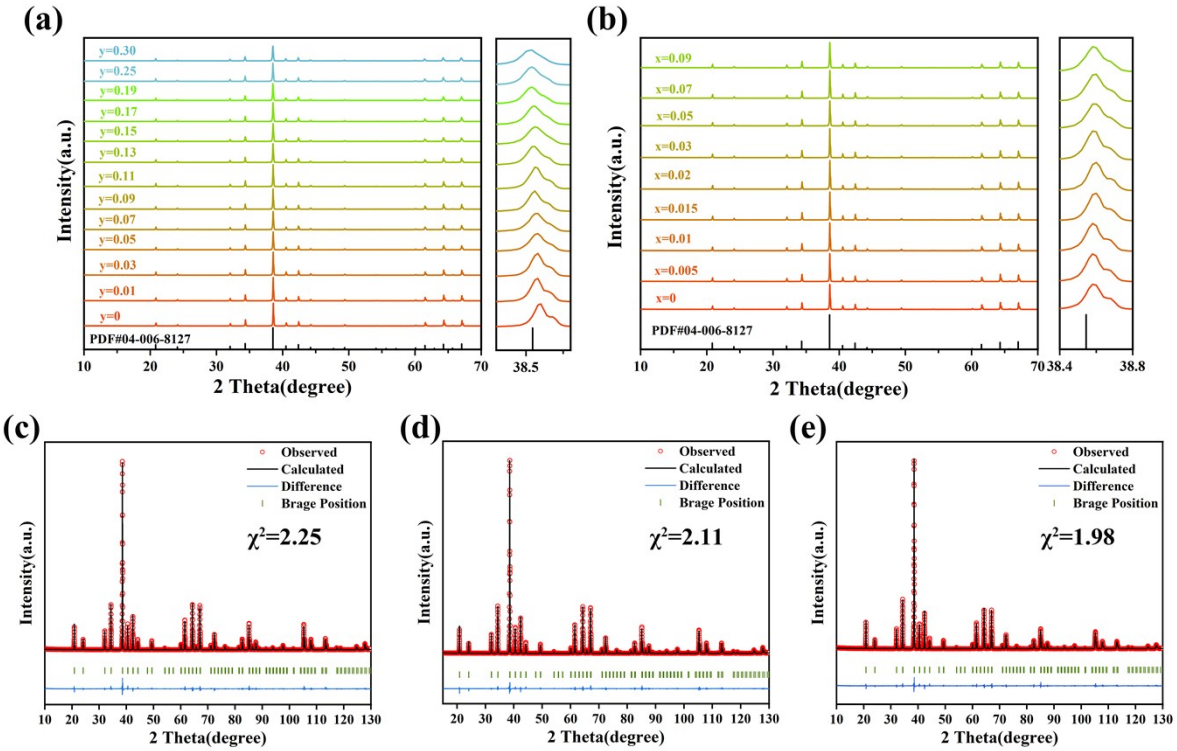

Figure S1. XRD patterns of a) CAGG:xCr^{3+}, 0.01Ni^{2+} ($0 \leq x \leq 0.30$) and b) CAGG:yNi^{2+} ($0 \leq y \leq 0.09$). Rietveld refinement of c) CAGG, d) CAGG:0.01Ni^{2+} and e) CAGG:0.15Cr^{3+}.

Table S1. Main parameters of Rietveld refinement of CAGG, CAGG:0.01Ni^{2+}, CAGG: 0.05Cr^{3+} and CAGG:0.15Cr^{3+},0.01Ni^{2+} samples.

Compound	CAGG	CAGG:0.01Ni^{2+}	CAGG: 0.15Cr^{3+}	CAGG: 0.15Cr^{3+},0.01Ni^{2+}
Space Group	*Ia*-3*d*	*Ia*-3*d*	*Ia*-3*d*	*Ia*-3*d*
Symmetry	Cubic	Cubic	Cubic	Cubic
$a = b = c$ (Å)	12.1192(1)	12.1200(1)	12.1272(1)	12.1283(1)
$\alpha = \beta = \gamma$ (°)	90.00	90.00	90.00	90.00
V (Å^3)	*1780*.01(3)	1780.34(4)	1783.54(4)	1784.01(4)
Al-O(Å)	1.9153	1.9209	1.9187	1.9222
R_p (%)	9.71	9.48	9.02	8.87
R_{wp} (%)	14.8	14.9	14.6	14.5
R_{exp} (%)	9.98	10.24	10.34	9.97
χ^2	2.25	2.11	1.98	2.13

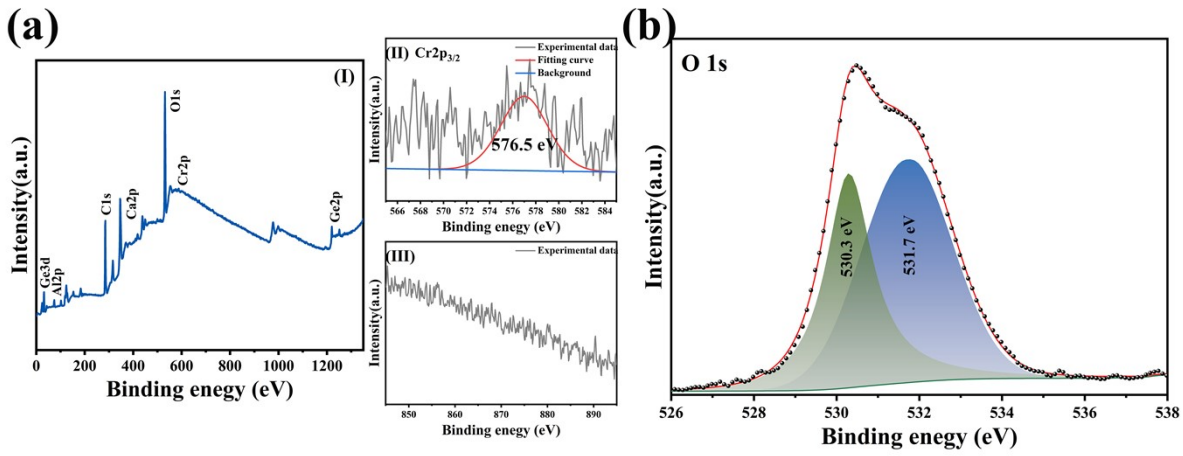

Figure S2. a) (I) XPS full spectrum for CAGG:0.15Cr^{3+},0.01Ni^{2+}, (II) XPS: Cr 2p spectrum and (III) XPS: Ni 2p spectrum. b) XPS: O 1s spectrum.

According to Kubelka-Munk function, the band gap energy (Eg) can be estimated using the following formulas (S1) and (S2): [1]

$$[F(R)hv]^n = A(hv - Eg) \qquad \text{* MERGEFORMAT (S1)}$$

$$F(R) = \frac{(1 - R)^2}{2R} \qquad \text{* MERGEFORMAT (S2)}$$

where R, F(R), hv, and A stand for relative reflectance, K-M function, specific phonon energy, and scale factor, respectively. And n = 2 for direct transition or n = 1/2 for indirect transition. This band structure of CAGG matrix is direct, and n = 2. The optical bandgap Eg can be determined by extrapolating the straight part of $[hvF(R)]^2$ to the hν plot associated with the energy axis.

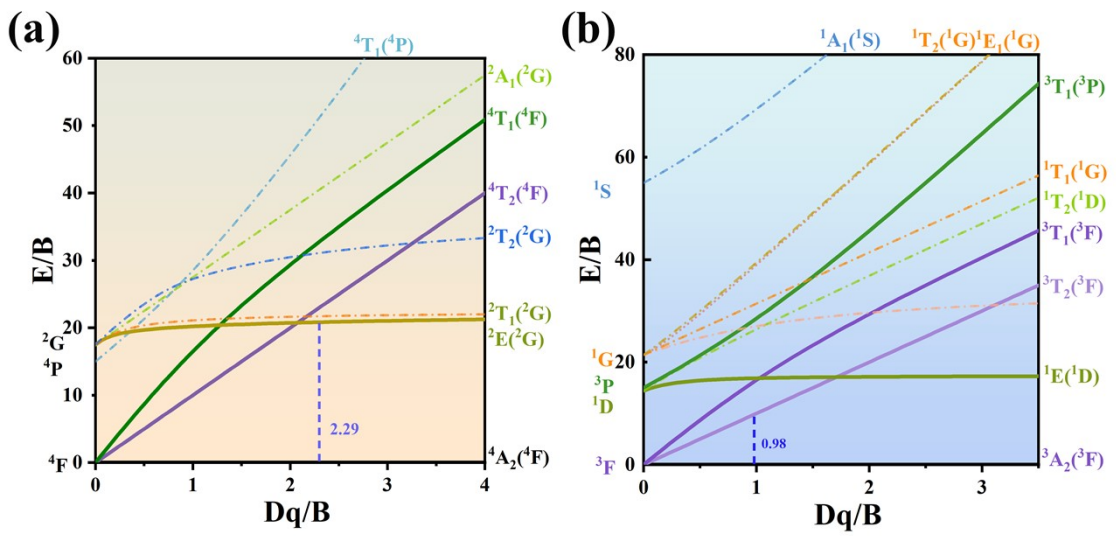

Figure S3. The T-S energy level diagram of a) $3d^3$ and b) $3d^8$ configuration in octahedral crystal field.

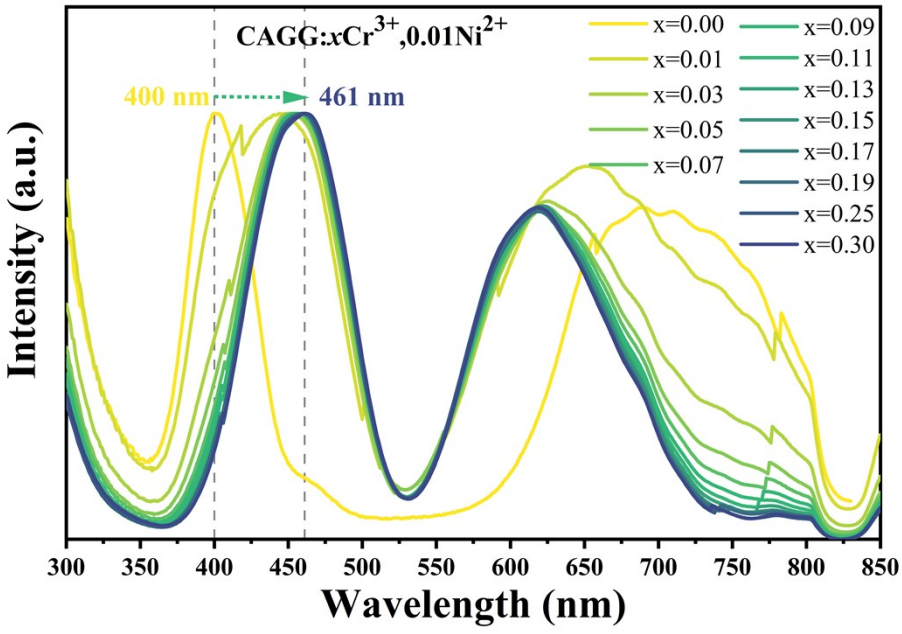

Figure S4. The normalized excitation spectra of CAGG:xCr^{3+}, 0.01Ni^{2+} monitored at 1423 nm.

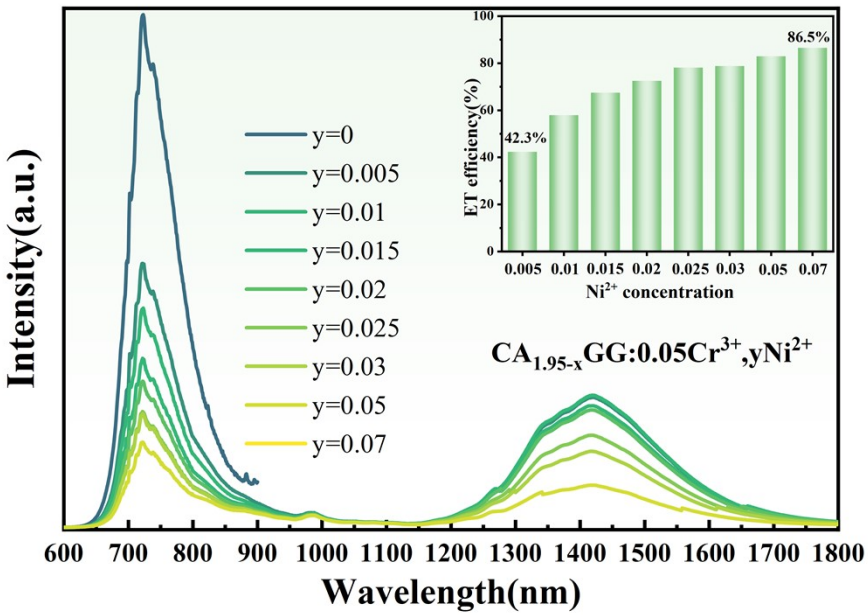

Figure S5. The emission specta of CAGG:0.05Cr^{3+}, $y$$Ni^{2+}$($y$=0~0.09) under 460 nm excitation.

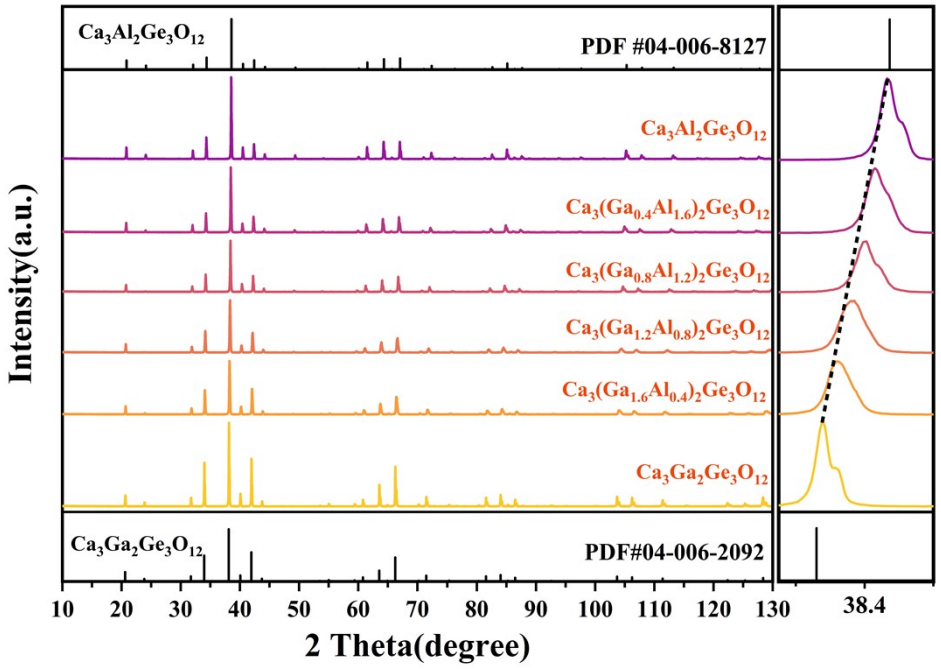

Figure S6. The XRD patterns of the $Ca_3(Ga_{1-z}Al_z)_2Ge_3O_{12}$:0.05$Cr^{3+}$($z$=0-1) samples

Table S2. Main parameters of rietveld refinement of $Ca_3(Ga_{1-z}Al_z)_2Ge_3O_{12}$:0.05$Cr^{3+}$ samples.

Compound	Z=0	Z=0.4	Z=0.8	Z=1.2	Z=1.6	Z=2.0
Space Group	*Ia*-3*d*	*Ia*-3*d*	*Ia*-3*d*	*Ia*-3*d*	*Ia*-3*d*	*Ia*-3*d*
Symmetry	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic
a (Å)	12.2543(1)	12.2251(1)	12.2002(1)	12.1702(1)	12.1466(1)	12.123(1)
$\alpha = \beta = \gamma$ (°)	90.00	90.00	90.00	90.00	90.00	90.00

V (Å^3)	1840.21(3)	1827.10(4)	1815.95(4)	1802.61(4)	1792.10(4)	1781.68(4)
Ga/Al-O(Å)	1.9896	1.9787	1.9584	1.9400	1.9290	1.9151
R_p (%)	8.39	9.34	9.00	9.99	9.49	11.00
R_{wp} (%)	13.5	14.4	13.7	15.0	14.5	15.6
R_{exp} (%)	9.14	10.15	10.28	11.25	10.43	10.36
χ^2	2.18	2.02	1.77	1.79	1.92	2.26

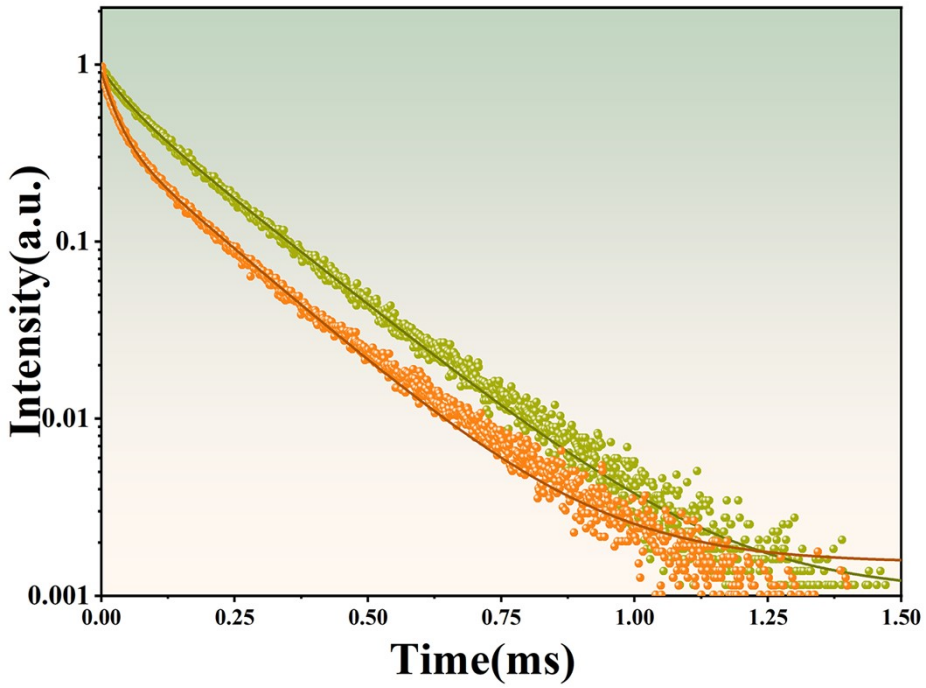

Figure S7. Lifetime and fitting curve of CAGG:0.15Cr^{3+} and CAGG: 0.15Cr^{3+}, 0.01Ni^{2+}

The fluorescence decay curves of CAGG:0.15Cr^{3+}, $y$$Ni^{2+}$ (y=0, 0.01) can be well-fitted by a double exponential function: [2]

$$I(t) = I_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \qquad \text{* MERGEFORMAT (S3)}$$

Where $I(t)$ represent the luminescence intensity as a function of time t. I_0 represents the original intensity，A_1 and A_2 are constants. τ_1 and τ_2 are the two components of the decay time. The average lifetime and ET efficiency can be calculated by the following equation:[2]

$$\tau_{ave} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \qquad \text{* MERGEFORMAT (S4)}$$

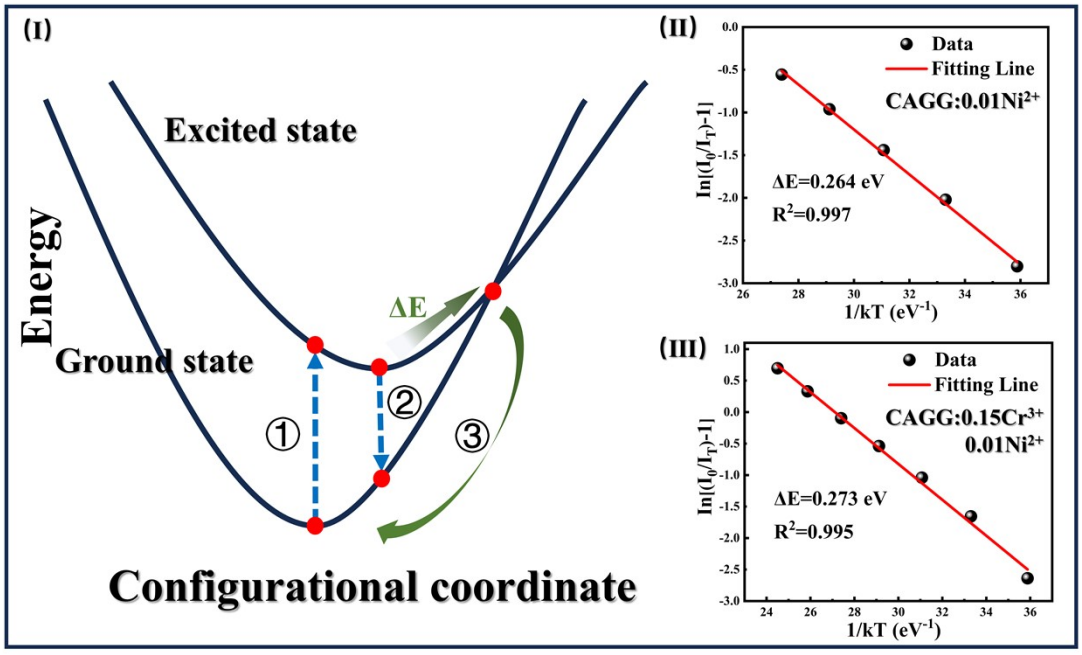

Figure S8. (I) Configurational coordinate diagram to illustrate thermal quenching behavior. The fitting results of the thermal activation energy to (II)CAGG:0.01Ni^{2+} and (III) CAGG:0.15Cr^{3+},0.01Ni^{2+}.

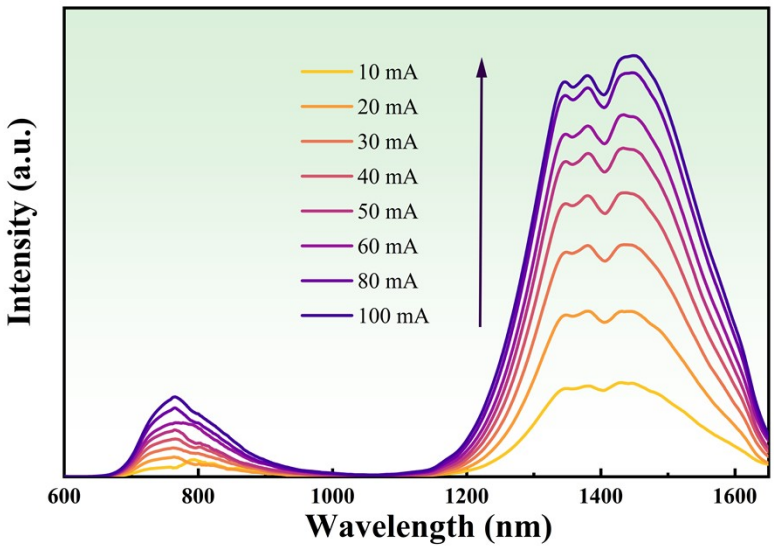

Figure S9. EL spectra of NIR pc-LEDs at different currents

(1) P. Makuła, M. Pacia, W. Macyk, How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV-Vis Spectra. J. *Phys. Chem. Lett.* **2018**, *9* (23), 6814. DOI: 10.1021/acs.jpclett.8b02892.

(2) Li, J.; Wang, C.; Niu, Y.; Wang, Y.; Wu, F.; Qi, z.; Teng, Y.; Dong, H.; Mu, Z. Efficient

Broad-Band NIR-II Emitting Phosphor $Mg_4Ta_2O_9$: Ni^{2+} with Satisfactory Thermal Stability of Luminescence. *Ceram. Int.* **2024**, *50* (11), 18647-18654. DOI: 10.1016/j.ceramint.2024.02.353.