

Supplementary Information

A Novel Broadband Near-infrared Fluoride Phosphor with Nearly 100% Internal Quantum Efficiency by Cationic Substitution Strategy

Tao Hu^{a*}, Zixuan Wu^b, Wei Lv^a, Yan Gao^a, Qingguang Zeng^a, Yayun Zhou^c, Xinxin Han^{b*},

^a*School of Applied Physics and Materials, Wuyi University, Jiangmen 529020, Guangdong Province, China.*

^b*School of Physical Science and Technology, State Key Laboratory of Featured Metal Materials and Life-cycle Safety for Composite Structures, Guangxi University, Nanning 530004, China.*

^c*Optoelectronic Engineering, Foshan University, Foshan, 528225 China.*

*Corresponding author: hutaowyu@sina.com; xxhan@gxu.edu.cn

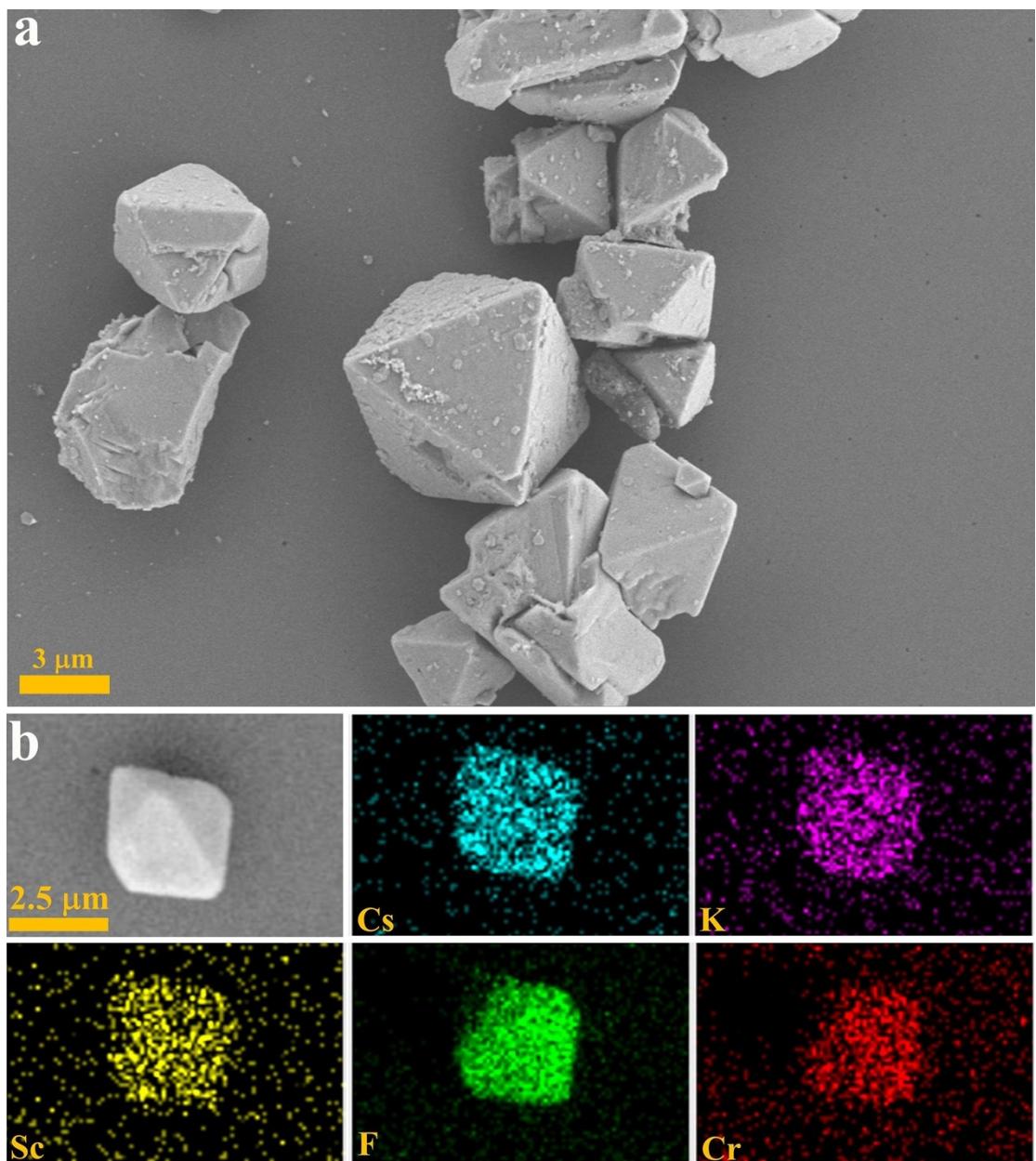


Figure S1. (a) SEM image of CKSF:0.07Cr³⁺. (b) SEM image of a single crystal and the component elemental maps of a CKSF:0.07Cr³⁺.

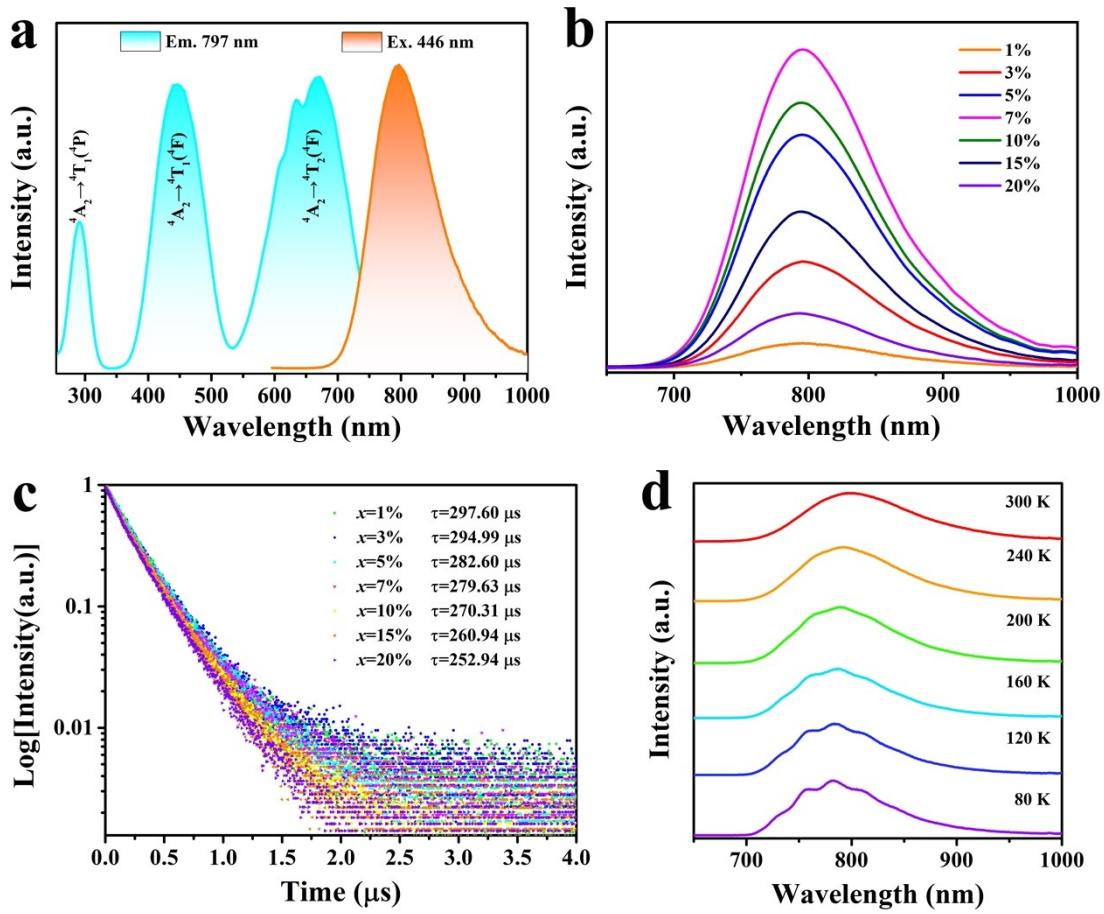


Figure S2. (a) Excitation/emission spectra of CKSF:0.07Cr³⁺. (b) The concentration-dependent emission spectra of CKSF:x0.07Cr³⁺ ($x=0.01-0.20$). (c) Decay curve of CKSF:x0.07Cr³⁺ ($x=0.01-0.20$). (d) CKSF:0.07Cr³⁺ emission spectra at low temperatures (80-300 K).

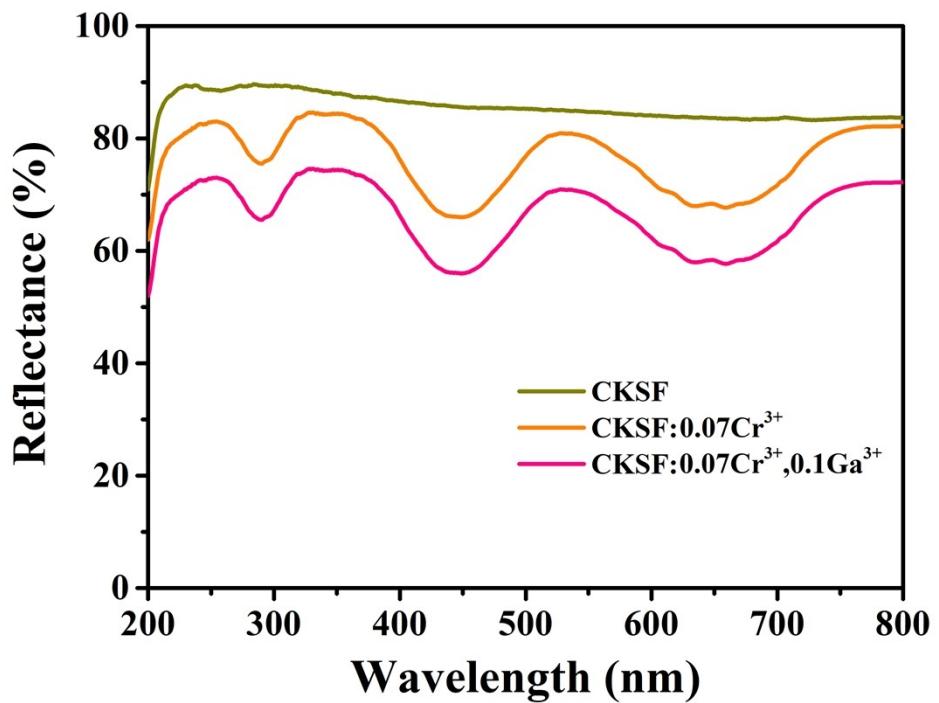


Figure S3. Diffuse reflectance spectroscopy of CKSF, CKSF:0.07Cr³⁺, and CKS_{0.83}G_{0.1}F:0.07Cr³⁺.

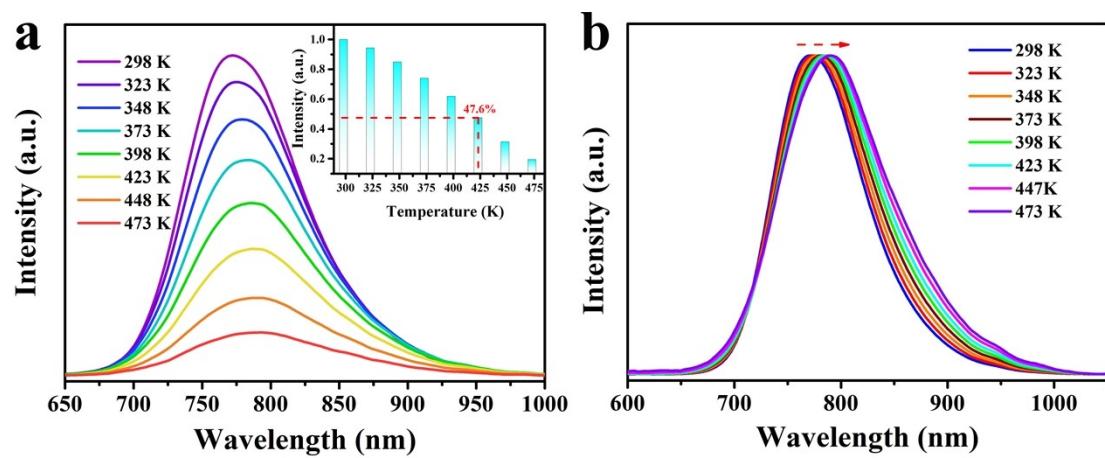


Figure S4. (a) Temperature-dependent emission spectra of CKSF:0.07Cr³⁺. Inset: dependence of temperature dependent integrated intensity. (b) Normalized temperature-dependent emission spectra of CKSF:0.07Cr³⁺.

Table S1 PL properties of some Cr³⁺-activated phosphors and photoelectric properties of the fabricated NIR pc-LEDs.

Phosphor	λ_{ex} (nm)	λ_{em} (nm)	I _{150°C} (%)	IQE (%)	Input power (mW)	NIR output power (mW)@photoelect ric efficiency	Ref
BaMgAl ₁₀ O ₁₇ :Cr ³⁺	398	762	63	94	-	3.4@-	1
InBO ₃ :Cr ³⁺	480	820	50	46.3	360	37.5@10.42%	2
LiScP ₂ O ₇ :Cr ³⁺	470	880	20	38	300	19@7%	3
YAl ₃ (BO ₃) ₄ :Cr ³⁺ , Yb ³⁺	450	-	80	-	300	26@8.6%	4
Ca ₂ LuZr ₂ Al ₃ O ₁₂ :Cr ³⁺	460	754	60	69	60	2.448@4.1%	5
NaInGe ₂ O ₆ :Cr ³⁺	480	900	25	34	-	25@4.85%	6
Ca ₉ Ga(PO ₄) ₇ :Cr ³⁺	440	735	68.5	55.7	-	-	7
Ca _{3-x} Lu _x Ga _{2+x} Ge _{3-x} O ₁₂ :Cr ³⁺	460	803	90	-	300	27.1@16.3%	8
ScBO ₃ :Cr ³⁺	450	800	51	65	371	26@7%	9
Ca ₃ Sc ₂ Si ₃ O ₁₂ :Cr ³⁺	460	770	97.4	92.3	2892	109.9@3.8%	10
K ₃ GaF ₆ :Cr ³⁺	442	750	-	28	1050	8@<1%	11
K ₃ ScF ₆ :Cr ³⁺	432	770	87.3	71.7	350	32.56564@9.315	12
Cs ₂ KGaF ₆ :Cr ³⁺	439	782	88.7	90.2	277.5	61.18@22.05%	13
K ₂ NaScF ₆ :Cr ³⁺	435	765	89.6	74	1094	159.72@14.6%	14
K ₂ NaInF ₆ :Cr ³⁺	439	774	78.3	70.2	817.1	72.97@8.93%	15
Cs ₂ KIn _{0.8} Al _{0.1} F ₆ :Cr ³⁺	447	794	71.6	88.06	1026	215.88@21.04%	16
ScF ₃ :Cr ³⁺	468	853	85.5	45	110	3.51@3.19%	17
Na ₃ ScF ₆ :Cr ³⁺	436	774	30	91.5	-	699.8@15.46%	18
Na ₃ GaF ₆ :Cr ³⁺ , Li ⁺	429	758	84.9	95.8	-	974.12@20.9%	19
Cs₂KSc_{0.83}Ga_{0.1}F₆:Cr³⁺	439	782	88.7	90.2	277.5	61.18@22.05%	This work

Table S3 Results of Dq/B of CKS_{0.83-y}G_yF:0.07Cr³⁺ ($y=0,0.1$).

Ga ³⁺ content	⁴ A ₂ → ⁴ T ₁ (⁴ F) λ (nm)	⁴ A ₂ → ⁴ T ₂ (⁴ F) λ (nm)	Dq/B
0	673	446	1.75
0.1	667	446	1.83

Table S3 Some photoelectric parameters of the fabricated NIR pc-LED under various driven currents.

Current (mA)	Input electrical power (mW)	NIR output power (mW)	Photoelectric conversion efficiency (%)
20	53	16.27	30.70
40	106	33.35	31.46
60	161	50.33	31.26
80	220	67.40	30.63
100	281	84.04	29.91
120	339	101.06	29.81
160	494	136.44	27.62
200	584	160.43	27.47
240	716	190.32	26.58
280	936	226.30	24.18
320	1017	252.11	24.79

References

- 1 You, L.; Tian, R.; Zhou, T.; Xie, R.-J. Broadband near-infrared phosphor BaMgAl₁₀O₁₇:Cr³⁺ realized by crystallographic site engineering. *Chemical Engineering Journal* **2021**, *417*, 129224.
- 2 Sun, Z.; Ning, Q.; Zhou, W.; Luo, J.; Chen, P.; Zhou, L.; Pang, Q.; Zhang, X. Structural and spectroscopic investigation of an efficient and broadband NIR phosphor InBO₃:Cr³⁺ and its application in NIR pc-LEDs. *Ceramics International* **2021**, *47* (10), 13598-13603.

- 3 Yao, L.; Shao, Q.; Han, S.; Liang, C.; He, J.; Jiang, J. Enhancing near-infrared photoluminescence intensity and spectral properties in Yb³⁺ codoped LiScP₂O₇:Cr³⁺. *Chemistry of Materials* **2020**, *32* (6), 2430-2439.
- 4 Wang, C.; Zhang, X.; Zhong, C.; Wu, X.; Xu, Y.; Yin, S.; Yang, Q.; Zhou, L.; You, H. Enhanced quantum efficiency and thermal stability by crystal-field engineering in a Y (Ga, Al)₃(BO₃)₄:Cr³⁺, Yb³⁺ phosphor for diverse short-wave infrared applications. *Journal of Materials Chemistry C* **2024**, *12* (10), 3515-3525.
- 5 He, S.; Zhang, L.; Wu, H.; Wu, H.; Pan, G.; Hao, Z.; Zhang, X.; Zhang, L.; Zhang, H.; Zhang, J. Efficient super broadband NIR Ca₂LuZr₂Al₃O₁₂:Cr³⁺,Yb³⁺garnet phosphor for pc-LED light source toward NIR spectroscopy applications. *Advanced Optical Materials* **2020**, *8* (6), 1901684.
- 6 Zhou, W.; Luo, J.; Fan, J.; Pan, H.; Zeng, S.; Zhou, L.; Pang, Q.; Zhang, X. Luminescent properties and LED application of broadband near-infrared emitting NaInGe₂O₆:Cr³⁺ phosphors. *Ceramics International* **2021**, *47* (18), 25343-25349.
- 7 Zhao, F.; Song, Z.; Liu, Q. Novel Cr³⁺-activated far-red emitting phosphors with β-Ca₃(PO₄)₂-type structure for indoor plant cultivation. *International Journal of Minerals, Metallurgy and Materials* **2022**, *29* (6), 1286-1294.
- 8 Lang, T.; Cai, M.; Fang, S.; Han, T.; He, S.; Wang, Q.; Ge, G.; Wang, J.; Guo, C.; Peng, L. Trade-off lattice site occupancy engineering strategy for near-infrared phosphors with ultrabroad and tunable emission. *Advanced Optical Materials* **2022**, *10* (2), 2101633.
- 9 Fang, M.-H.; Huang, P.-Y.; Bao, Z.; Majewska, N.; Lesniewski, T.; Mahlik, S.; Grinberg, M.; Leniec, G.; Kaczmarek, S. M.; Yang, C.-W. Penetrating biological tissue using light-emitting diodes with a highly efficient near-infrared ScBO₃: Cr³⁺ phosphor. *Chemistry of Materials* **2020**, *32* (5), 2166-2171.
- 10 Zhou, Y.; Li, X.; Seto, T.; Wang, Y. A high efficiency trivalent chromium-doped near-infrared-emitting phosphor and its NIR spectroscopy application. *ACS Sustainable Chemistry & Engineering* **2021**, *9* (8), 3145-3156.
- 11 Li, H.; Wang, J.; Liang, Y.; Zhang, H.; Zhu, X.; Wang, Z.; Cheng, X. Effect of Temperature and Pressure on Luminescence Properties of K₃GaF₆:Cr³⁺ Phosphor. *Optical Materials* **2024**, 115683.

- 12 Yu, H.; Chen, J.; Mi, R.; Yang, J.; Liu, Y.-g. Broadband near-infrared emission of $K_3ScF_6:Cr^{3+}$ phosphors for night vision imaging system sources. *Chemical Engineering Journal* **2021**, *417*, 129271.
- 13 Wu, Z.; Han, X.; Wang, J.; Zhou, Y.; Xing, K.; Cao, S.; Zhao, J.; Zou, B.; Zeng, R. Highly efficient and thermally stable broadband near-infrared emitting fluoride $Cs_2KGaF_6:Cr^{3+}$ for multiple LED applications. *Journal of Materials Chemistry C* **2022**, *10* (28), 10292-10301.
- 14 Song, E.; Ming, H.; Zhou, Y.; He, F.; Wu, J.; Xia, Z.; Zhang, Q. Cr³⁺-Doped Sc-based fluoride enabling highly efficient near infrared luminescence: a case study of $K_2NaScF_6:Cr^{3+}$. *Laser & Photonics Reviews* **2021**, *15* (2), 2000410.
- 15 Wu, Z.; Han, X.; Zhou, Y.; Xing, K.; Cao, S.; Chen, L.; Zeng, R.; Zhao, J.; Zou, B. Efficient broadband near-infrared luminescence of Cr³⁺ doped fluoride K_2NaInF_6 and its NIR-LED application toward veins imaging. *Chemical Engineering Journal* **2022**, *427*, 131740.
- 16 Duan, Y.; Liu, Y.; Zhang, G.; Yao, L.; Shao, Q. Broadband Cr³⁺-sensitized upconversion luminescence of $LiScSi_2O_6:Cr^{3+}/Er^{3+}$. *Journal of Rare Earths* **2021**, *39* (10), 1181-1186.
- 17 Lin, Q.; Wang, Q.; Liao, M.; Xiong, M.; Feng, X.; Zhang, X.; Dong, H.; Zhu, D.; Wu, F.; Mu, Z. Trivalent chromium ions doped fluorides with both broad emission bandwidth and excellent luminescence thermal stability. *ACS Applied Materials & Interfaces* **2021**, *13* (15), 18274-18282.
- 18 He, F.; Song, E.; Zhou, Y.; Ming, H.; Chen, Z.; Wu, J.; Shao, P.; Yang, X.; Xia, Z.; Zhang, Q. A general ammonium salt assisted synthesis strategy for Cr³⁺-doped hexafluorides with highly efficient near infrared emissions. *Advanced Functional Materials* **2021**, *31* (36), 2103743.
- 19 He, F.; Song, E.; Chang, H.; Zhou, Y.; Xia, Z.; Zhang, Q. Interstitial Li⁺ occupancy enabling radiative/nonradiative transition control toward highly efficient Cr³⁺-based near-infrared luminescence. *ACS Applied Materials & Interfaces* **2022**, *14* (27), 31035-31043.