

Supporting Information

High-efficient and thermal-stable broadband NIR phosphor by rationally bridging Cr³⁺-Yb³⁺ in LiScGe₂O₆ for optical bioimaging

Chuanlong Wang^a, Yahong Jin^{a,*}, Lifang Yuan^b, Bo Wang^c, Ruiting Zhang^a, Haoyi Wu^a, Qing Yao^a, and Yihua Hu^{a,*}

^aSchool of Physics and Optoelectronic Engineering, Guangdong University of Technology, WaiHuan Xi Road, No. 100, Guangzhou 510006, P. R. China

^bSchool of Electronics and Communications, Guangdong Mechanical & Electrical College of Technology, Guangzhou 510515, P. R. China

^cSchool of Applied Physics and Materials, Wuyi University, Jiangmen 529020, P. R. China

*Corresponding authors

E-mail: yhj@gdut.edu.cn; huyh@gdut.edu.cn

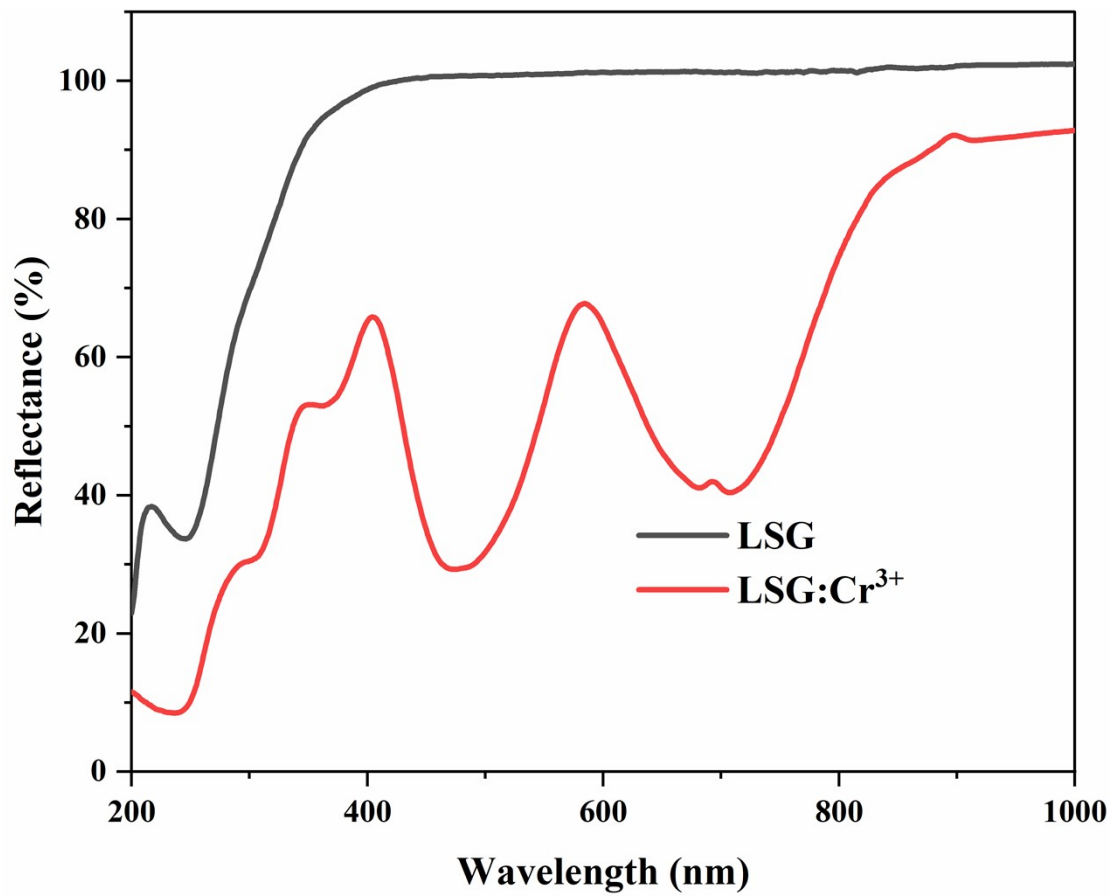


Fig. S1. DRS of LSG host and LSG:0.07Cr³⁺.

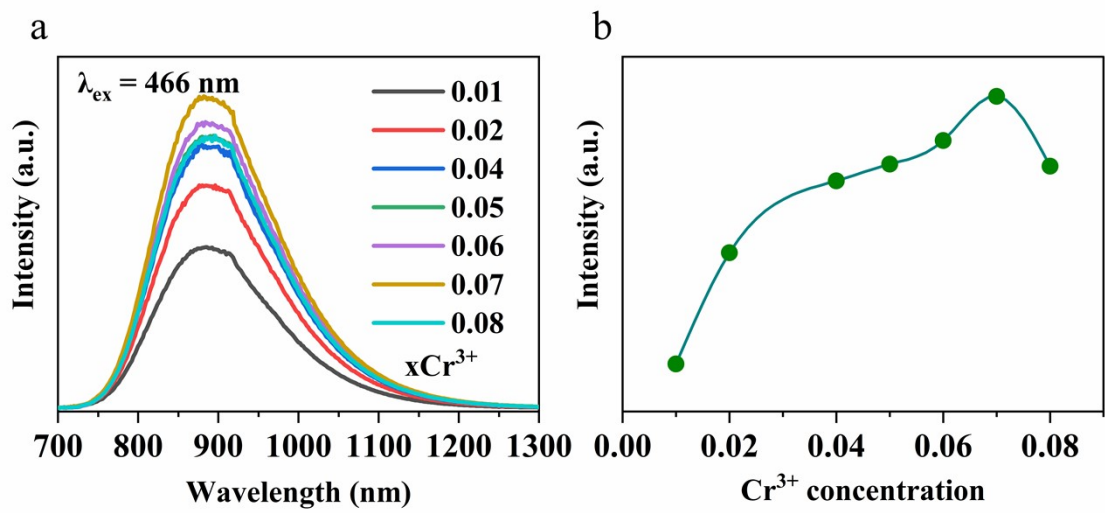


Fig. S2. (a) PL spectra of LSG:xCr³⁺ (x = 0.01-0.08). (b) Emission intensities of Cr³⁺ as a function of Cr³⁺ doping concentration.

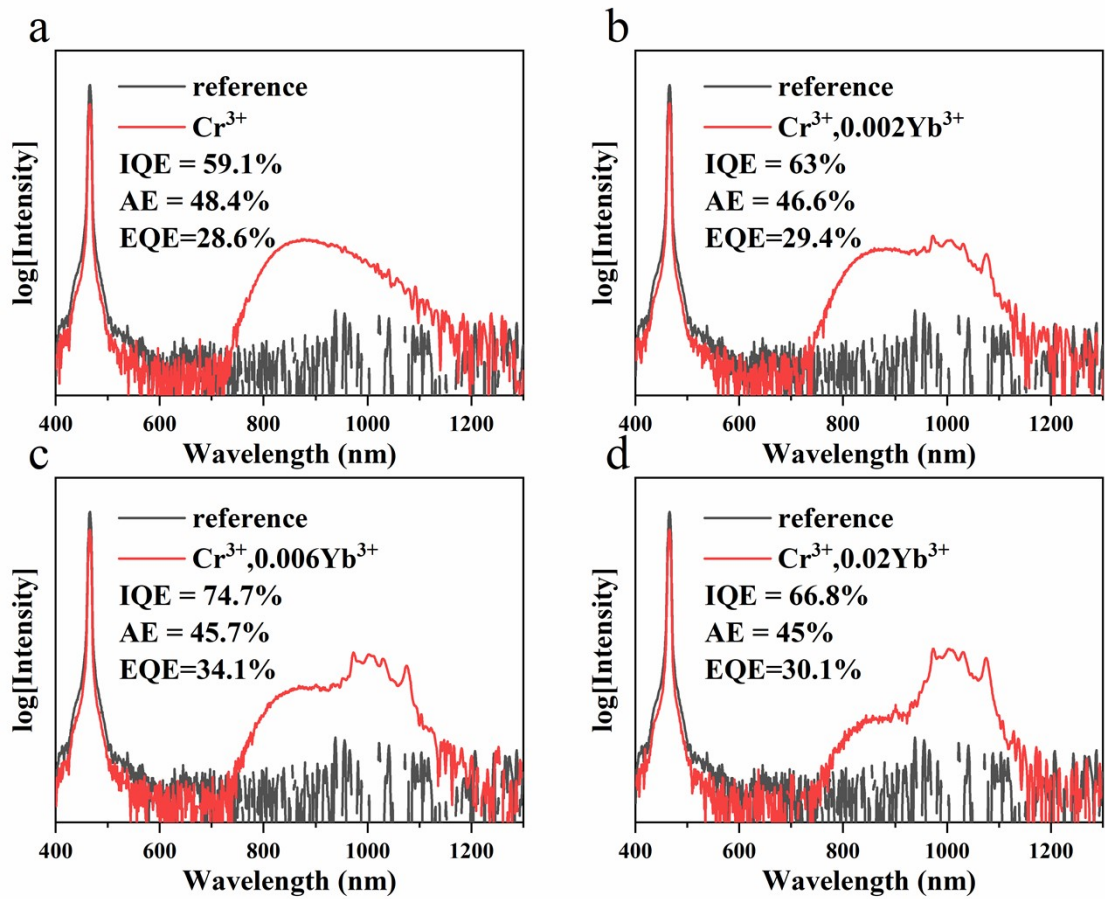


Fig. S3. IQE, AE and EQE of LSG:0.07Cr³⁺, yYb³⁺ (y = 0, 0.002, 0.006, and 0.02).

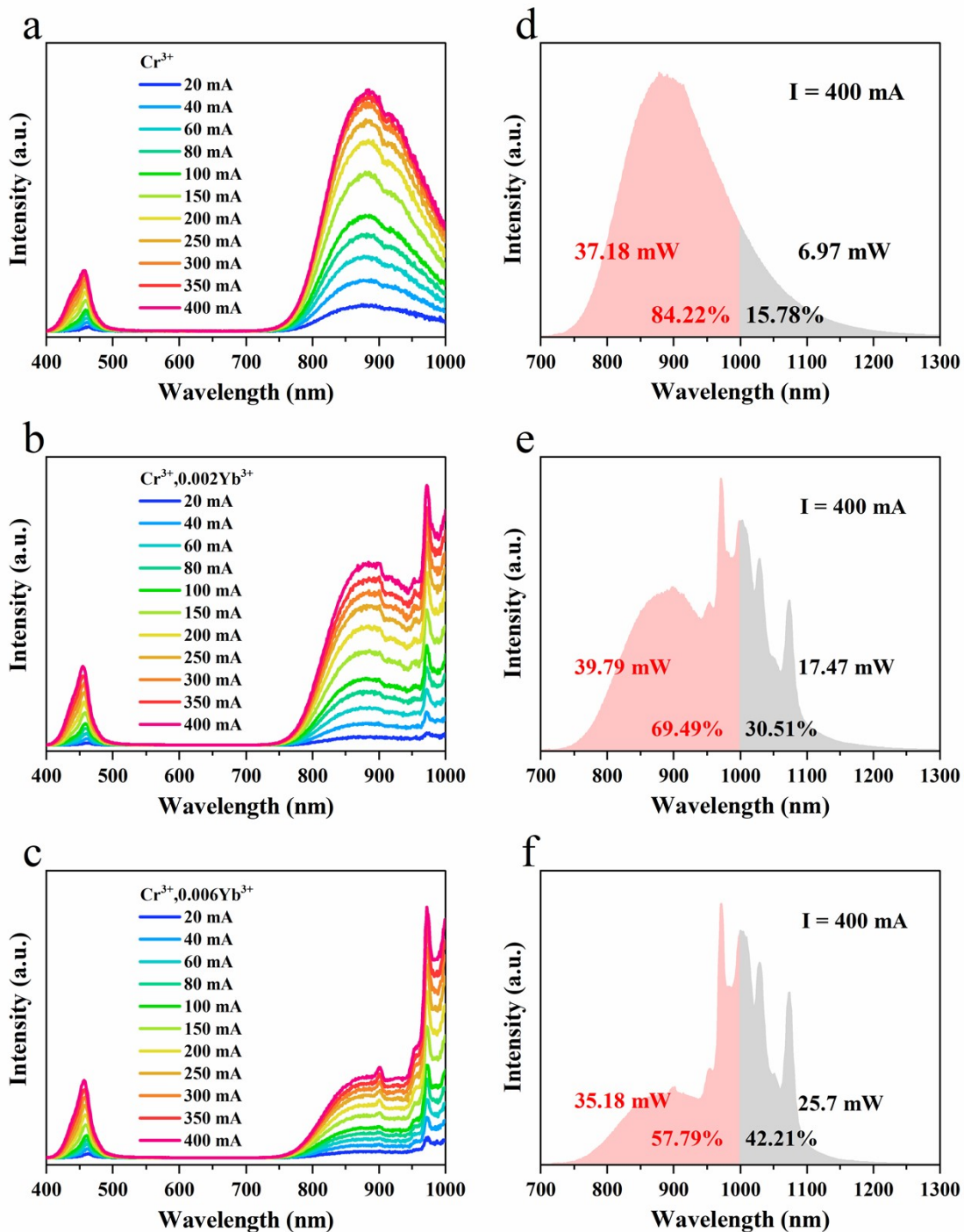


Fig. S4. (a-c) The electroluminescence spectra of the as-obtained NIR pc-LED based on LSG:0.07Cr³⁺, yYb³⁺ (y = 0, 0.002, 0.006) at various driven currents. (d-f) The corresponding NIR output power at 400 mA based on PL spectra of LSG:0.07Cr³⁺, yYb³⁺ (y = 0, 0.002, and 0.006). The integrated emission intensity ratios of 700-1000 nm and 1000-1300 nm of the as-obtained NIR pc-LED based on LSG:0.07Cr³⁺, yYb³⁺ (y = 0,

0.002, and 0.006) are calculated to be 84.22:15.78, 69.49:30.51 and 57.79:42.21, respectively.

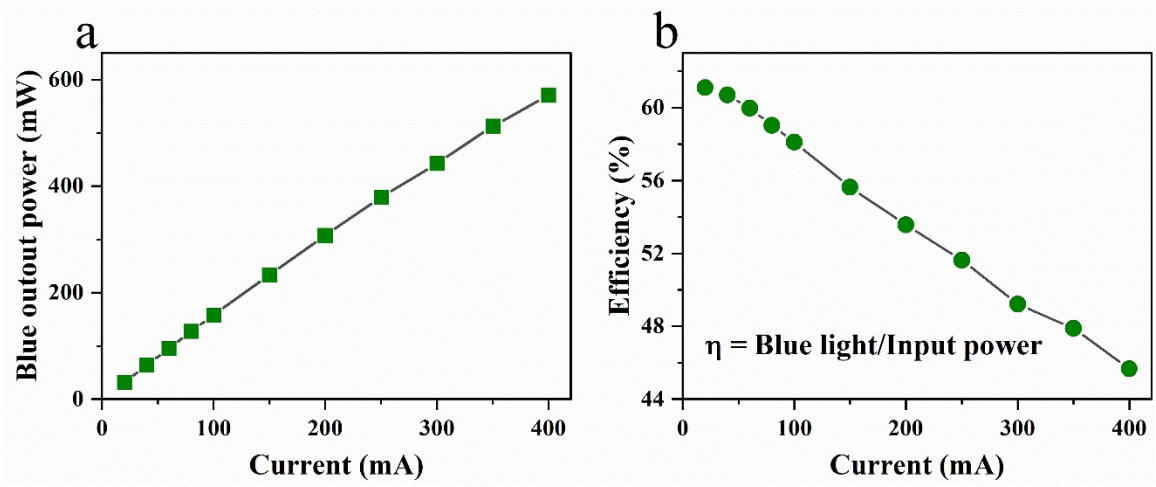


Fig. S5. (a) Output power of the 460 nm blue LED chip at different input currents. (b) Photoelectric conversion efficiency of the 460 nm LED chip as a function of driven current.

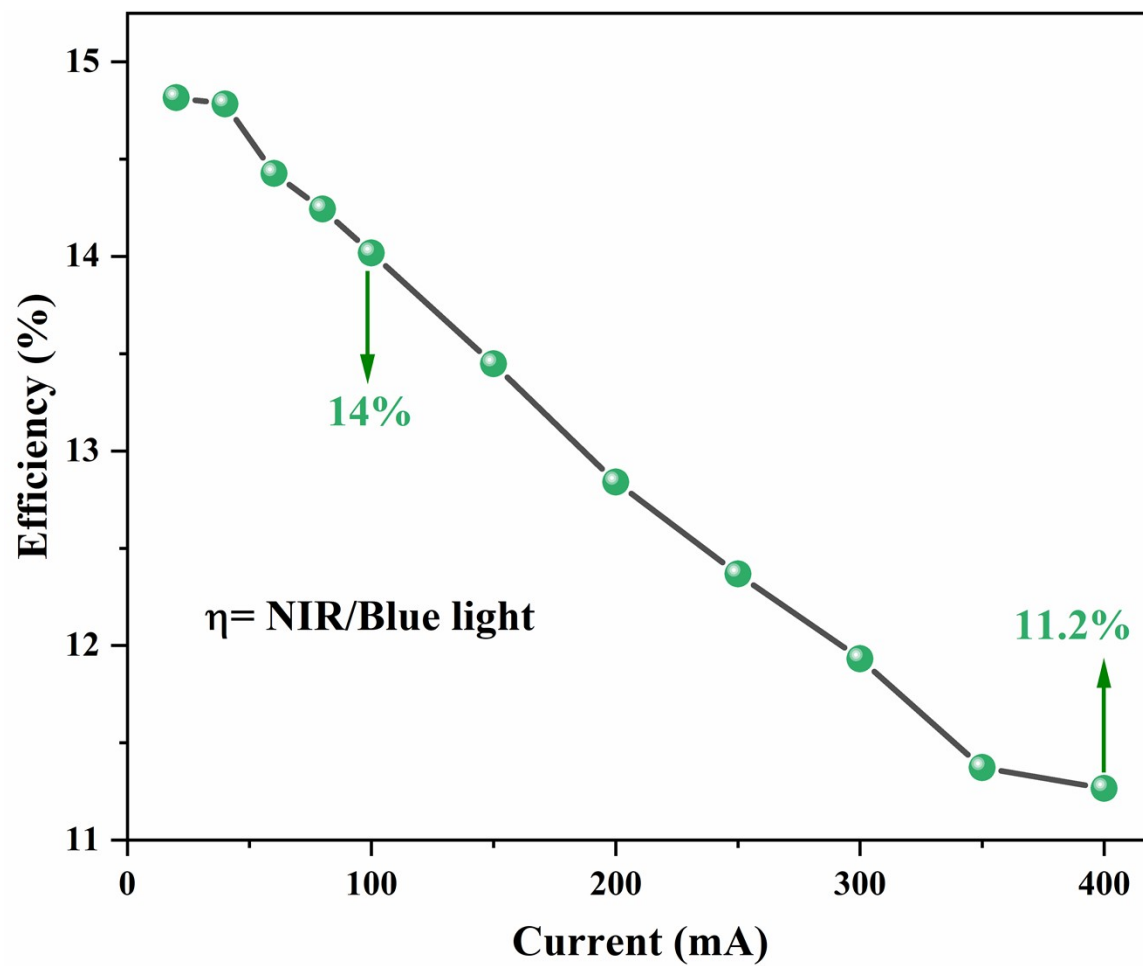


Fig. S6. The conversion efficiency of Blue to NIR light as a function of driven current.

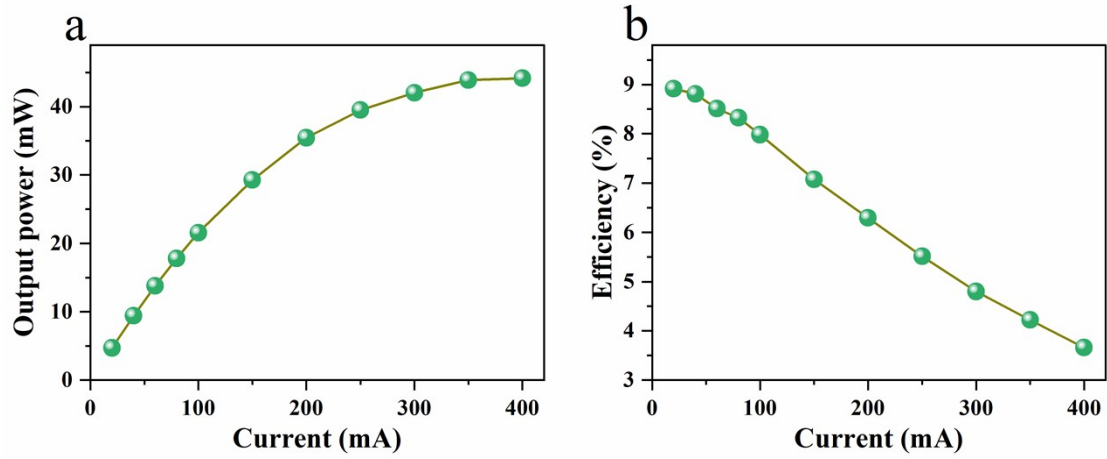


Fig. S7. (a) NIR output power and (b) photoelectric conversion efficiency of the fabricated pc-LED (by using LSG:0.07Cr³⁺ phosphor) as a function of driven current.

Table S1. IQE, EQE, thermal stability (using the percentage of remaining emission intensity at 100 °C (or 150 °C) of the room-temperature value as a measure), and photoelectric parameters of some previously reported Cr³⁺-activated and Cr³⁺-Yb³⁺ co-activated phosphors with emission peak exceeding 830 nm.

Phosphor	Peak position (nm)	IQE (%)	EQE (%)	I _{100°C} (or I _{150°C}) (%)	NIR output power		Ref.
					(mW)@current	(mA)@ efficiency	
LiScGeO ₄ :Cr ³⁺	1120	26	-	30 ₁₀₀	4.78@60@4.4%		1
LiIn ₂ SbO ₆ :Cr ³⁺	970	7	3.44	10 ₁₀₀	-		2
CaSc _{0.85} Al _{1.15} SiO ₆ :Cr ³⁺	950	30	9.3	77 ₁₀₀	-		3
Mg ₂ GeO ₄ :Cr ³⁺	940	48.19	16.38	-	-		4
NaInGe ₂ O ₆ :Cr ³⁺	900	34	-	55 ₁₀₀	25.2@120@4.5%		5
NaScGe ₂ O ₆ :Cr ³⁺	895	40.22	-	20 ₁₅₀	12.07@350@-		6
LiScP ₂ O ₇ :Cr ³⁺	880	38	20	42 ₁₀₀	19@100@7%		7
LiInGe ₂ O ₆ :Cr ³⁺	880	81.2	39.8	45 ₁₀₀	-		8
Y _{0.57} La _{0.72} Sc _{2.71} (BO ₃) ₄ :Cr ³⁺	850	41.1	-	42 ₁₀₀	17.61@300@-		9
Sr ₉ Ga _{0.2} (PO ₄) ₇ :0.8Cr ³⁺	850	66.3	29.9	-	19.79@150@4.23		10
Ga ₄ GeO ₈ :Cr ³⁺	850	60	27	73 ₁₀₀	55.94@400@3.8%		11
La(Sc, Ga) ₃ B ₄ O ₁₂ :Cr ³⁺	850	52.12	-	55 ₁₅₀	-		12
LiGaP ₂ O ₇ :Cr ³⁺	846	47.8	28.3	51 ₁₀₀	28.1@120@7.8%		13
BaZrGe ₃ O ₉ :Cr ³⁺	830	-	-	53 ₁₅₀	6.45@320@0.6%		14
Ca ₄ ZrGe ₃ O ₁₂ :Cr ³⁺ , Yb ³⁺	840, 968	25.5	-	73 ₁₀₀	-		15
LiInP ₂ O ₇ :Cr ³⁺ , Yb ³⁺	860, 1000	27.5	10.8	50 ₁₀₀	6.24@100@2.2%		16
LiIn ₂ SbO ₆ :Cr ³⁺ , Yb ³⁺	973	10	4.76	30 ₁₀₀	2.74@180@-		2
LSG:Cr ³⁺ , Yb ³⁺	880, 980	76.3	36.2	86 ₁₀₀	22.19@100@8.22%		This work
					31.43@150@7.59%		
					52.86@300@6.02%		
					64.26@400@5.32%		

Table S2. Photoelectric parameters of the fabricated NIR pc-LED with LSG:0.07Cr³⁺ under various currents.

Current (mA)	Input electrical power (mW)	NIR output power (mW) (700-1000 nm)	NIR output power (mW) (700-1300 nm)	Photoelectric conversion efficiency (%)
20	51.32	3.85	4.57	8.91
40	104.3	7.74	9.19	8.81
60	158.4	11.35	13.48	8.51
80	213.7	14.98	17.78	8.32
100	269.8	18.14	21.53	7.98
150	414	24.67	29.29	7.05
200	563.2	29.86	35.45	6.29
250	716.3	33.26	39.49	5.51
300	876.3	35.41	42.04	4.79
350	1040	36.97	43.89	4.22
400	1208	37.19	44.15	3.65

Table S3. Photoelectric parameters of the fabricated NIR pc-LED with LSG:0.07Cr³⁺, 0.002Yb³⁺ under various currents.

Current (mA)	Input electrical power (mW)	NIR output power (mW) (700-1000 nm)	NIR output power (mW) (700-1300 nm)	Photoelectric conversion efficiency (%)
20	51.19	3.12	4.48	8.76
40	104.1	6.32	9.09	8.73
60	158.2	9.30	13.78	8.46
80	213.4	12.17	17.51	8.20
100	269.4	14.88	21.41	7.94
150	413.4	20.95	30.14	7.29
200	562.4	26.28	37.81	6.72
250	716.4	30.88	44.43	6.20
300	874.9	34.09	49.05	5.60
350	1038	37.33	53.71	5.17
400	1206	39.80	57.27	4.74

Table S4. Photoelectric parameters of the fabricated NIR pc-LED with LSG:0.07Cr³⁺, 0.006Yb³⁺ under various currents.

Current (mA)	Input electrical power (mW)	NIR output power (mW) (700-1000 nm)	NIR output power (mW) (700-1300 nm)	Photoelectric conversion efficiency (%)
20	51.19	2.66	4.60	8.99
40	104.1	5.37	9.30	8.83
60	158.3	7.94	13.74	8.68
80	213.4	10.39	17.98	8.42
100	269.6	12.67	21.92	8.13
150	413.6	18.00	31.15	7.53
200	562.6	22.37	38.71	6.88
250	716.5	26.34	45.58	6.36
300	876	29.48	51.01	5.82
350	1038	33.4	57.80	5.56
400	1207	35.19	60.89	5.04

Table S5. Photoelectric parameters of the fabricated NIR pc-LED with LSG:0.07Cr³⁺, 0.01Yb³⁺ under various currents.

Current (mA)	Input electrical power (mW)	NIR output power (mW) (700-1000 nm)	NIR output power (mW) (700-1300 nm)	Photoelectric conversion efficiency (%)
20	51.22	2.34	4.64	9.06
40	104.2	4.73	9.39	9.01
60	158.5	6.94	13.78	8.69
80	213.6	9.11	18.10	8.47
100	269.8	11.17	22.19	8.22
150	414.6	15.82	31.43	7.59
200	563.4	19.87	39.47	7.01
250	718.4	23.59	46.86	6.53
300	877.2	26.61	52.86	6.02
350	1041	29.37	58.34	5.60
400	1209	32.35	64.26	5.32

References

- 1 S. Miao, Y. Liang, Y. Zhang, D. Chen and X. Wang, Broadband short-wave infrared light-emitting diodes based on Cr³⁺-doped LiScGeO₄ phosphor, *ACS Appl. Mater. Inter.*, 2021, **13**, 36011-36019.
- 2 G. Liu, T. Hu, M. S. Molokeev and Z. Xia, Li/Na substitution and Yb³⁺ co-doping enabling tunable near-infrared emission in LiIn₂SbO₆:Cr³⁺ phosphors for light-emitting diodes, *iScience*, 2021, **24**, 102250.
- 3 G. Liu, M. S. Molokeev and Z. Xia, Structural rigidity control toward Cr³⁺-based broadband near-infrared luminescence with enhanced thermal stability, *Chem. Mater.*, 2022, **34**, 1376-1384.
- 4 H. Cai, S. Liu, Z. Song and Q. Liu, Tuning luminescence from NIR-I to NIR-II in Cr³⁺-doped olivine phosphors for nondestructive analysis, *J. Mater. Chem. C*, 2021, **9**, 5469-5477.
- 5 W. Zhou, J. Luo, J. Fan, H. Pan, S. Zeng, L. Zhou, Q. Pang and X. Zhang, Luminescent properties and LED application of broadband near-infrared emitting NaInGe₂O₆: Cr³⁺ phosphors, *Ceram. Int.*, 2021, **47**, 25343-25349.
- 6 X. Zhou, W. Geng, J. Li, Y. Wang, J. Ding and Y. Wang, An ultraviolet-visible and near-infrared-responded broadband NIR phosphor and its NIR spectroscopy application, *Adv. Opt. Mater.*, 2020, **8**, 1902003.
- 7 L. Yao, Q. Shao, S. Han, C. Liang, J. He and J. Jiang, Enhancing near-infrared photoluminescence intensity and spectral properties in Yb³⁺ codoped LiScP₂O₇:Cr³⁺, *Chem. Mater.*, 2020, **32**, 2430-2439.
- 8 T. Liu, H. Cai, N. Mao, Z. Song and Q. Liu, Efficient near-infrared pyroxene phosphor LiInGe₂O₆:Cr³⁺ for NIR spectroscopy application, *J. Am. Ceram. Soc.*, 2021, **104**, 4577-4584.
- 9 H. Wu, L. Jiang, K. Li, C. Li and H. Zhang, Design of broadband near-infrared Y_{0.57}La_{0.72}Sc_{2.71}(BO₃)₄:Cr³⁺ phosphors based on one-site occupation and their application in NIR light-emitting diodes, *J. Mater. Chem. C*, 2021, **9**, 11761-11771.
- 10 F. Zhao, H. Cai, Z. Song and Q. Liu, Structural confinement for Cr³⁺ activators toward efficient Near-Infrared phosphors with suppressed concentration quenching, *Chem. Mater.*, 2021, **33**, 3621-3630.
- 11 L. Yao, Q. Shao, M. Shi, T. Shang, Y. Dong, C. Liang, J. He and J. Jiang, Efficient ultra-broadband Ga₄GeO₈:Cr³⁺ phosphors with tunable peak wavelengths from 835 to 980 nm for NIR pc-LED application, *Adv. Opt. Mater.*, 2022, **10**, 2102229.
- 12 T. Gao, W. Zhuang, R. Liu, Y. Liu, C. Yan and X. Chen, Design of a broadband NIR phosphor for security-monitoring LEDs: Tunable photoluminescence properties and enhanced thermal stability, *Cryst. Growth Des.*, 2020, **20**, 3851-3860.
- 13 C. Yuan, R. Li, Y. Liu, L. Zhang, J. Zhang, G. Leniec, P. Sun, Z. Liu, Z. Luo, R. Dong and J. Jiang, Efficient and Broadband LiGaP₂O₇:Cr³⁺ Phosphors for Smart Near-Infrared Light-Emitting Diodes, *Laser Photonics Rev.*, 2021, **15**, 2100227.

- 14 D.J. Hou, H. Lin, Y. Zhang, J. Li, H. Li, J. Dong, Z. Lin and R. Huang, A broadband near-infrared phosphor $\text{BaZrGe}_3\text{O}_9:\text{Cr}^{3+}$: luminescence and application for light-emitting diodes, *Inorg. Chem. Front.*, 2021, **8**, 2333-2340.
- 15 J. Xiang, J. Zheng, X. Zhao, X. Zhou, C. Chen, M. Jin and C. Guo, Synthesis of broadband NIR garnet phosphor $\text{Ca}_4\text{ZrGe}_3\text{O}_{12}:\text{Cr}^{3+}, \text{Yb}^{3+}$ for NIR pc-LED applications, *Mater. Chem. Front.*, 2022, **6**, 440-449.
- 16 H. Zhang, J. Zhong, X. Zhang, H. Yang, Z. Mu and W. Zhao, Achieving an ultra-broadband infrared emission through efficient energy transfer in $\text{LiInP}_2\text{O}_7:\text{Cr}^{3+}, \text{Yb}^{3+}$ phosphor, *J. Alloys Compd.*, 2022, **894**, 162386.