Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Spectrally tunable and thermally stable near-infrared luminescence in $Na_3Sc_2(PO_4)_3:Cr^{3+}$ phosphor by Ga^{3+} co-doping for light-emitting diodes

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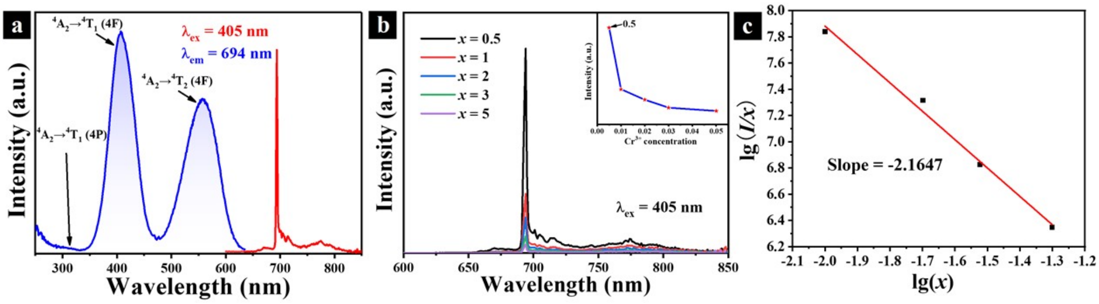

Fig. S1 (a) The luminescence spectra of $Na_3Sc_{1.995}(PO_4)_3$:0.5%Cr^{3+} at room temperature, PL excitation (blue curve, em = 694 nm), and PL emission (red curve, ex = 405 nm). (b) PL spectra of $Na_3Sc_2(PO_4)_3$:x%Cr^{3+} (x = 0.5, 1, 2, 3, 5). Inset: the integral PL intensity as a function of Cr^{3+} concentration. (c) The relationships of lg(x) versus lg(I/x).

The emission intensity (I) can be calculated based on the following Eq.:

$$\frac{I}{x} = K\left[1+\beta(x)^{\theta/3}\right]^{-1} \tag{1}$$

Where I is the emission intensity, x is the concentration of the activator ions above the quenching concentration, β and K are constant for the same excitation conditions, and θ is the function of multipole-multipole interaction for 6 (dipole-dipole), 8 (dipole-quadrupole) or 10 (quadrupole-quadrupole). To get a correct θ value for the two emission centers, the dependence of lg(I/x) on lg(x) is plotted, and it yield a straight line with a slope equal to -θ/3.

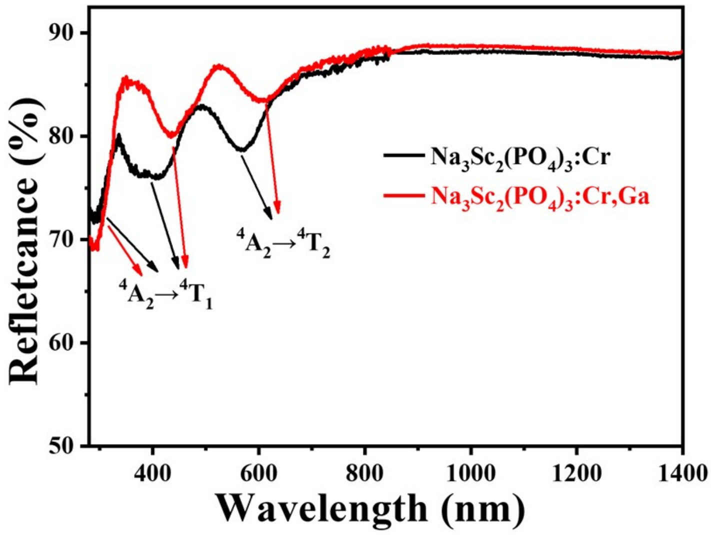

Fig. S2 The diffuse reflectance spectra of $Na_3Sc_{1.995}(PO_4)_3$:0.5%Cr^{3+} and $Na_3Sc_{1.936}(PO_4)_3$:0.5%Cr^{3+},6%Ga^{3+} phosphors.

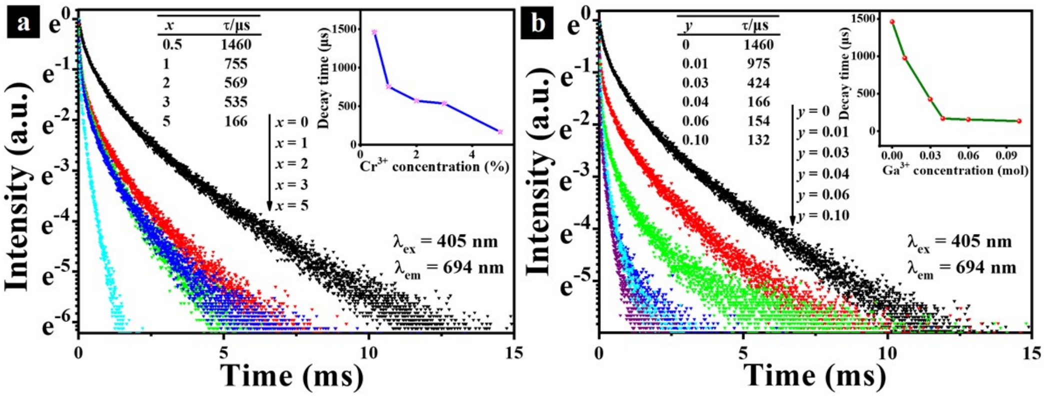

Fig. S3 (a) Decay curves of Cr^{3+} emission in $Na_3Sc_2(PO_4)_3$:x%Cr^{3+} phosphors under excitation at 405 nm, monitored at 694 nm. Inset: dependence of the fluorescence lifetime of the Cr^{3+} in $Na_3Sc_2(PO_4)_3$:x%Cr^{3+} samples. (b) Decay curves of Cr^{3+} emission in $Na_3Sc_{1.995}(PO_4)_3$:0.5%Cr^{3+},$y$$Ga^{3+}$ phosphors under excitation at 405 nm, monitored at 694 nm. Inset is the dependence of the fluorescence lifetime.

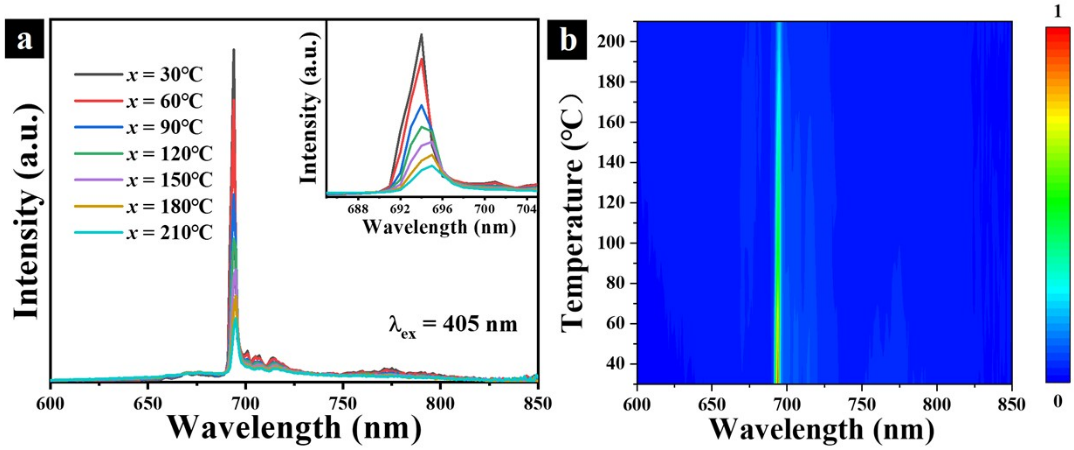

Fig. S4 (a) The temperature-dependent emission spectra of $Na_3Sc_{1.995}(PO_4)_3$:0.5%Cr^{3+} phosphor. Inset: magnified PL spectra for the phosphor. (b) Thermal quenching behavior of $Na_3Sc_{1.995}(PO_4)_3$:0.5%Cr^{3+} phosphor.

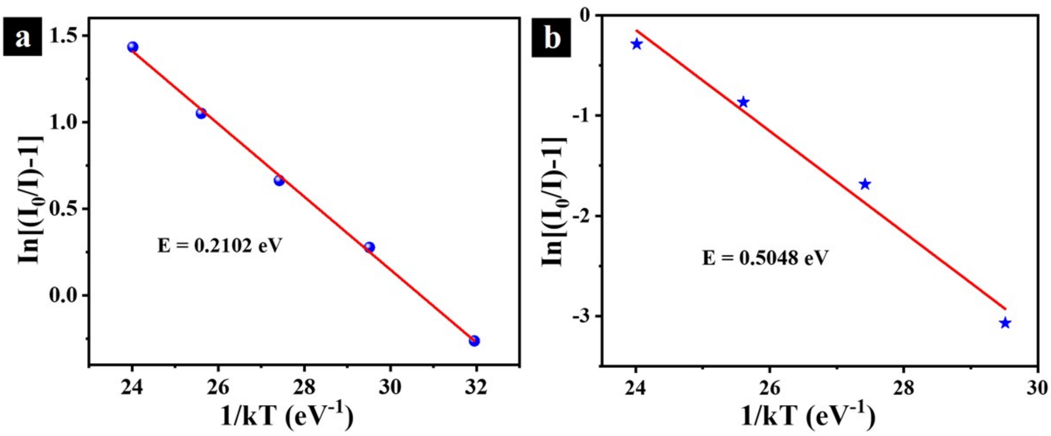

Fig. S5 The plot of ln[$(I_0/I)^{-1}$] versus 1/kT for (a) $Na_3Sc_{1.995}(PO_4)_3$:0.5%Cr^{3+} and (b) $Na_3Sc_{1.935}(PO_4)_3$:0.5%Cr^{3+},6%Ga^{3+}.

The activation energy ΔE can be calculated by the following equation:

$$I_T = \frac{I_0}{1 + c\exp(-\frac{\Delta E}{kT})} \quad (2)$$

where I_0 and I_T are the initial PL intensity of the samples at room temperature and different temperatures, respectively. T is the temperature, c is a constant, and k is the Boltzmann constant (8.629×10^{-5} eV/k). On the basis of Eq. 2, ΔE values of $Na_3Sc_{1.995}(PO_4)_3$:0.5%Cr^{3+} and $Na_3Sc_{1.935}(PO_4)_3$:0.5%Cr^{3+},0.06Ga^{3+} samples were estimated to be 0.2102 eV and 0.5048 eV, respectively.

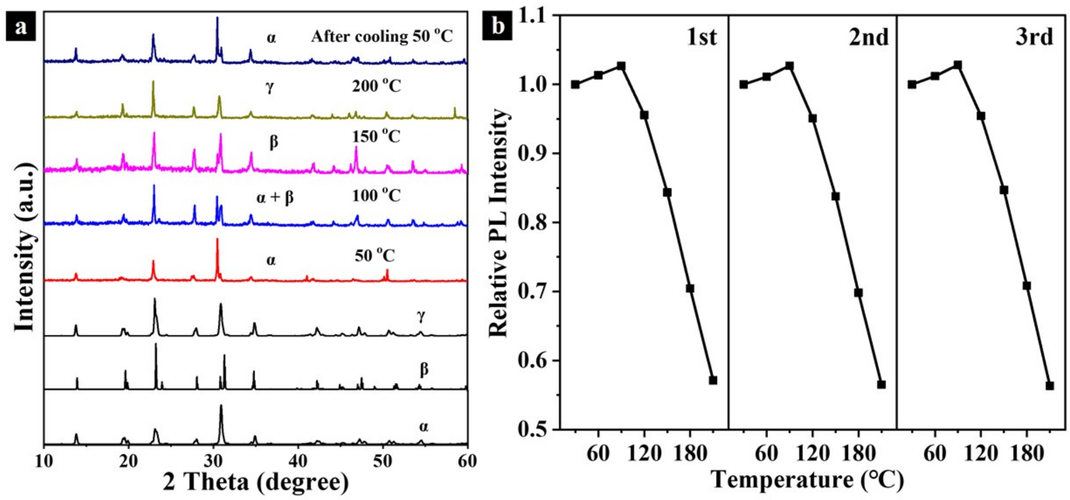

Fig. S6 (a) Temperature-dependent XRD pattern of $Na_3Sc_2(PO_4)_3:Cr^{3+},Ga^{3+}$ upon heating from 50 °C to 200 °C, and subsequent cooling to 50 °C. (b) The NIR photoluminescence performance of the phosphor as a function of temperature in three continuous heating and cooling cycles.

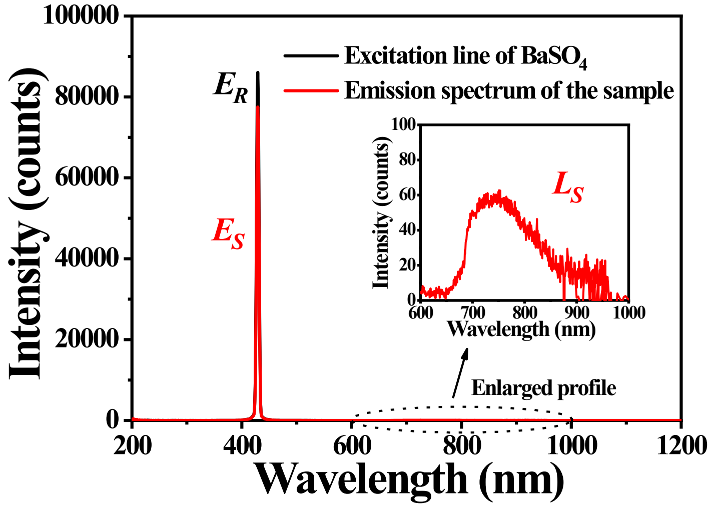

Fig. S7 Excitation line of $BaSO_4$ and emission spectrum of the optimized $Na_3Sc_{1.935}(PO_4)_3$:0.5%Cr^{3+},6%Ga^{3+} phosphor collected using an integrating sphere. The inset shows a magnification of the emission spectrum.

The internal quantum efficiency can be calculated by the following equation:

$$\eta_{QE} = \frac{\int L_S}{\int E_R - \int E_S} \tag{3}$$

where E_R is the spectrum of the excitation light without the sample in the sphere, E_S is the spectrum of the light used for exciting the sample, and L_S is the emission spectrum of the studied sample.

Table S1 Crystal data of $Na_3Sc_{1.995}(PO_4)_3$:0.5%Cr^{3+} from the Rietveld refinement.

Formula	$Na_3Sc_2(PO_4)_3$			
Crystal system	Monoclinic			
Space group	*Cc* (9)			
Cell parameters	*a* = 15.397403(19) Å, *b* = 9.09743(13) Å, *c* = 8.92197(12) Å			
	Alpha = 90	Beta = 90	Gamma = 123.5242	
Cell volume	*V* =1041.866(25) $Å^3$			
Z	4			
Reliability factors	R_p = 6.35%, R_{wp} = 9.10% and χ^2 = 3.946			
Atom	x/a	y/b	z/c	Ui/Ue*100
Na1	0.19057	0.56128	0.16133	7.51
Na2	-0.00899	0.24198	0.38908	2.21
Na3	0.32806	0.31874	0.43476	1.32
P1	0.35427	0.26239	0.1185	1.33
P2	0.63855	0.74757	0.90216	1.24
P3	-0.00085	0.26211	0.05146	3.1
Sc1	0.0927	0.05147	0.24633	0.36
Sc2	0.89912	0.95325	0.75619	0.67
O1	0.16044	0.25889	0.44442	0.79
O2	0.86519	0.80546	0.57284	-0.16
O3	0.42228	0.06125	0.43755	4.55
O4	0.54767	0.88674	0.52352	3.47
O5	0.25451	0.20212	0.16944	-0.77
O6	0.73609	0.75452	0.79514	7.58
O7	0.37914	0.11548	0.11356	1.77
O8	0.63792	0.90244	0.85804	0.97
O9	0.45444	0.43081	0.15533	0.96
O10	0.57988	0.59369	0.81486	-0.62
O11	0.07291	0.2451	0.13881	-0.59
O12	0.91068	0.73952	0.83909	2.89

Table S2 Crystal data of $Na_3Sc_{1.935}(PO_4)_3$:0.5%Cr^{3+},6%Ga^{3+} from the Rietveld refinement.

Formula	$Na_3Sc_2(PO_4)_3$			
Crystal system	Monoclinic			
Space group	*Cc* (9)			
Cell parameters	a = 15.39403(17) Å, b = 9.09798(11) Å, c = 8.92108(12) Å			
	Alpha = 90	Beta = 90	Gamma = 123.5100(5)	
Cell volume	V =1041.768(25) Å^3			
Z	4			
Reliability factors	R_p = 6.38%, R_{wp} = 8.97% and χ^2 = 4.058			

Atom	x/a	y/b	z/c	Ui/Ue*100
Na1	0.18809	0.54859	0.15213	2.08
Na2	-0.00714	0.23281	0.39182	1.6
Na3	0.32559	0.31666	0.41911	1.05
P1	0.35998	0.26154	0.11203	0.42
P2	0.6455	0.74375	0.90086	1.08
P3	-0.00314	0.24309	0.04272	-0.01
Sc1	0.09777	0.04797	0.24648	-0.1
Sc2	0.90385	0.95092	0.7548	0.02
O1	0.15404	0.23208	0.44791	0.73
O2	0.86742	0.79905	0.57658	-0.22
O3	0.42643	0.07518	0.45543	2.73
O4	0.54368	0.91131	0.54575	-0.01
O5	0.26301	0.22285	0.18432	-0.32
O6	0.74358	0.7867	0.81998	0.58
O7	0.37525	0.10699	0.11478	-1.15
O8	0.63087	0.89298	0.84591	1.63
O9	0.44186	0.43643	0.18213	-1.38
O10	0.56596	0.58745	0.81881	1.32
O11	0.0756	0.24367	0.14791	-0.61
O12	0.91641	0.75479	0.85905	0.38

Table S3. The detailed analysis of decay curves for $Na_3Sc_2(PO_4)_3$:*x*%Cr^{3+}, $Na_3Sc_{1.995}(PO_4)_3$:0.5%Cr^{3+}, *y*Ga^{3+} and $Na_3Sc_{1.935}(PO_4)_3$:0.5%Cr^{3+}, 6%Ga^{3+} phosphors.

$Na_3Sc_2(PO_4)_3$:*x*%Cr^{3+}, monitored at 694nm					
x	τ_1 (μs)	τ_2 (μs)	*A1*	*A2*	τ (μs)
0.5	241	1705	0.5574	0.3932	1460
1	53	849	0.6086	0.2841	755
2	57	663	0.6344	0.2938	569
3	45	623	0.6654	0.2724	535
5	16	189	0.6172	0.3460	166
$Na_3Sc_{1.995}(PO_4)_3$:0.5%Cr^{3+}, *y*Ga^{3+}, monitored at 694 nm					
y	τ_1 (μs)	τ_2 (μs)	*A1*	*A2*	τ (μs)
0	241	1705	0.5574	0.3932	1460
0.01	61	1065	0.4489	0.2611	975
0.03	17	473	0.6852	0.2021	424
0.04	14	216	0.8181	0.1580	166
0.06	26	210	0.7848	0.2240	154
0.10	43	195	0.7084	0.2215	132
$Na_3Sc_{1.935}(PO_4)_3$:0.5%Cr^{3+}, 6%Ga^{3+}, monitored at 750 nm					
T (°C)	τ_1 (μs)	τ_2 (μs)	*A1*	*A2*	τ (μs)
30	6.77	69.17	0.7226	0.2149	53.72
60	6.30	58.98	0.7235	0.2310	45.78
90	5.86	48.48	0.7196	0.2560	37.68
120	5.26	38.74	0.6968	0.2808	30.29
150	4.68	30.57	0.6889	0.3037	23.90
180	3.85	23.12	0.6840	0.3261	18.13
210	3.14	17.97	0.6928	0.3273	13.96

Table S4. Output power and photoconversion efficiency values of NIR LEDs.

Current (mA)	Intensity, *Im* (mW)	Photoconversion efficiency (%)
20	1.24	2.4
40	2.50	2.4
60	4.04	2.6
80	5.30	2.4
100	6.54	2.4
120	7.90	2.4
160	10.46	2.4
200	13.08	2.4
240	15.46	2.2
280	17.70	2.2
320	19.68	2.0