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

Supporting Information

Tunable ultra-broadband full-visible-spectral emission of Bi^{3+} doped aluminate phosphors enabled by structure transformation and site occupancy engineering

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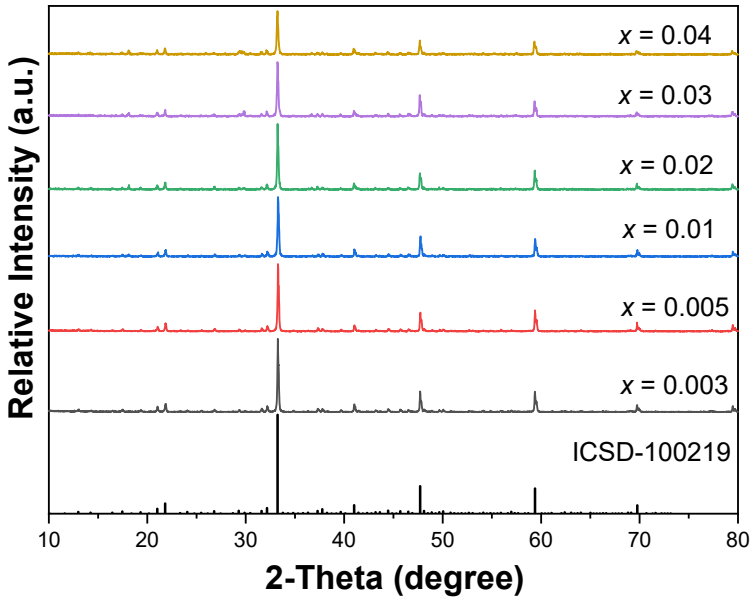

Figure S1 XRD patterns for $Na_{0.625}Ca_{8.688-x}Al_6O_{18}$: xBi^{3+} ($0.003 \leq x \leq 0.04$) with different Bi^{3+} doing. contents

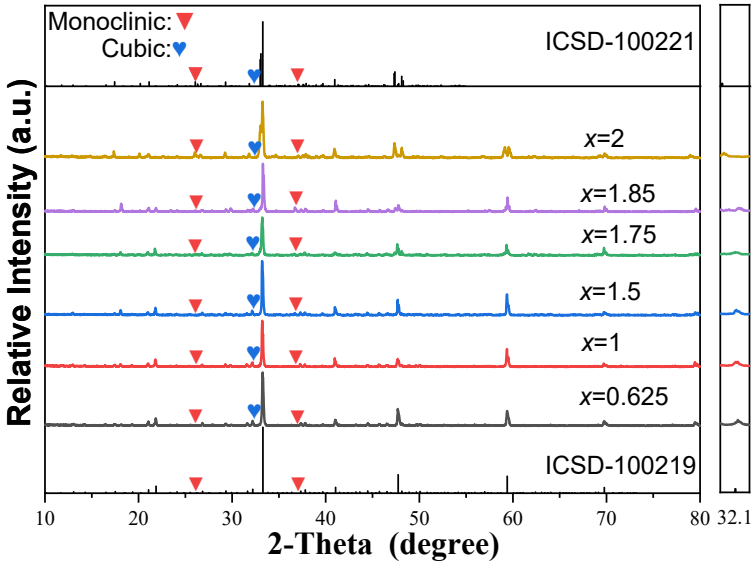

Figure S2 XRD patterns for $Na_yCa_{8.98-y/2}Al_6O_{18}$: $0.02Bi^{3+}$ ($0.625 \leq y \leq 2$).

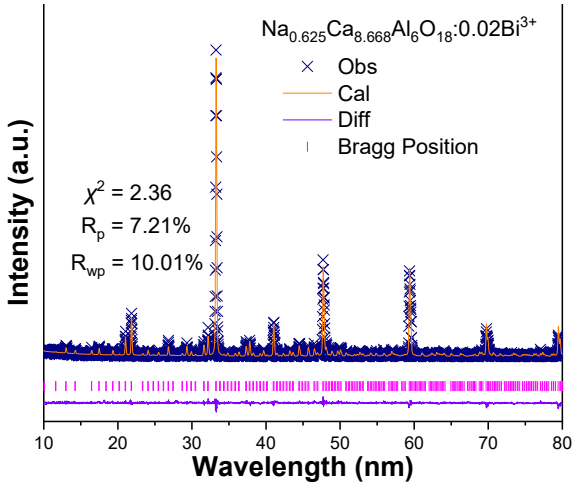

Figure S3 X-ray diffraction Rietveld refinement of the $Na_{0.625}Ca_{8.668}Al_6O_{18}$:0.02$Bi^{3+}$

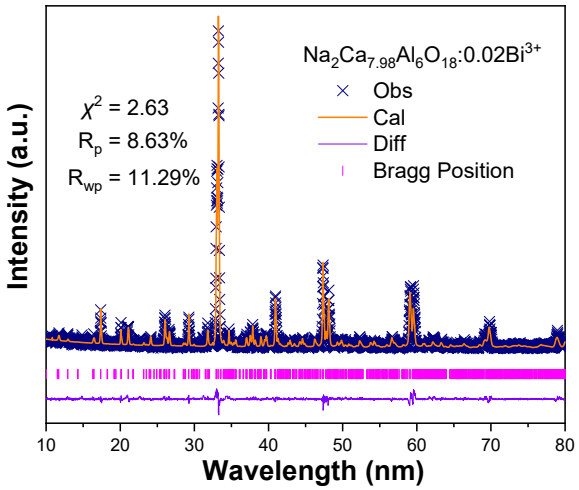

Figure S4 X-ray diffraction Rietveld refinement of the $Na_2Ca_{7.98}Al_6O_{18}$:0.02Bi^{3+}

Table S1 The crystallographic parameters of $Na_{0.625}Ca_{8.668}Al_6O_{18}$:0.02$Bi^{3+}$

$Na_{0.625}Ca_{8.668}Al_6O_{18}$:0.02$Bi^{3+}$	
Crystal system	Cubic
Space group	$P2_13$
Lattice parameters	a=b=c=15.236 Å α=β=γ=90°
Unit cell volume	V=3536.82 Å
χ^2	2.36
R_P	7.21 %
R_{wp}	10.01 %

Table S2 The crystallographic parameters of $Na_2Ca_{7.98}Al_6O_{18}$:0.02Bi^{3+}

$Na_2Ca_{7.98}Al_6O_{18}$:0.02Bi^{3+}	
Crystal system	Monoclinic
Space group	$P2_1/c$
Lattice parameters	a=10.874 Å b=10.849 Å c=15.130 Å α=β=γ=90°
Unit cell volume	V=1784.92 Å
χ^2	2.63
R_P	8.63 %
R_{wp}	11.29 %

Table S3 The lattice, site occupation and isotropic displacement parameters of $Na_{0.625}Ca_{8.668}Al_6O_{18}$:0.02$Bi^{3+}$

Atom	Occup.	*x*	*y*	*z*	Uiso
Ca1	0.9982	0	0	0	0.0015
Ca2	0.9979	0.5018	0.5018	0.5018	0.0021
Ca3	0.9080	0.2630	0.2630	0.2630	0.0041
Na1	0.090	0.2630	0.2630	0.2630	0.0044
Ca4	0.729	-0.2562	-0.2562	-0.2562	0.0072
Na2	0.270	-0.2562	-0.2562	-0.2562	0.0081
Ca5	0.966	0.3814	0.3814	0.3814	0.0041
Na3	0.030	0.3814	0.3814	0.3814	0.0157
Ca6	0.759	-0.3763	-0.3763	-0.3763	0.0041
Na4	0.240	-0.3763	-0.3763	-0.3763	0.0012
Ca7	0.498	0.3720	0.1400	0.1361	0.0344
Ca8	0.499	0.3678	0.1262	0.1345	0.0421
Ca9	0.497	0.6232	0.1376	0.1180	0.0013
Ca10	0.499	0.6431	0.1363	0.1287	0.0016
Ca11	0.998	0.3824	0.3863	0.1213	0.0032
Ca12	0.997	-0.3800	-0.3881	-0.1201	0.0057
Na5	0.310	0.1210	0.1210	0.1210	0.0247
Na6	0.310	0.8750	0.8750	0.8750	0.0024
Al1	1.000	0.2539	0.0134	0.0167	0.0058
Al2	1.000	-0.2534	-0.0129	-0.0232	0.0048
Al3	1.000	0.2434	0.2371	0.0053	0.0068
Al4	1.000	-0.2445	-0.2377	-0.0063	0.0055
O1	1.000	0.2630	0.1264	0.0029	0.0236
O2	1.000	-0.2658	-0.1258	-0.0230	0.0369

O3	1.000	0.4759	0.1327	0.2475	0.0113
O4	1.000	-0.4952	-0.1310	-0.2368	0.0195
O5	1.000	0.2729	0.2765	0.1082	0.0175
O6	1.000	-0.2629	-0.2906	-0.1058	0.0187
O7	1.000	0.2406	0.4114	0.3040	0.0160
O8	1.000	-0.2281	-0.4062	-0.2878	0.0156
O9	1.000	0.3502	-0.0321	-0.0274	0.0138
O10	1.000	-0.3505	0.0233	0.0234	0.0199
O11	1.000	0.1497	-0.0173	-0.0171	0.0129
O12	1.000	-0.1515	0.0150	0.0163	0.0075
Bi1	0.002	0	0	0	0.0009
Bi2	0.002	0.5018	0.5018	0.5018	0.0011
Bi3	0.002	0.2630	0.2630	0.2630	0.0031
Bi4	0.001	-0.2562	-0.2562	-0.2562	0.0023
Bi5	0.001	0.3814	0.3814	0.3814	0.0025
Bi6	0.001	-0.3763	-0.3763	-0.3763	0.0032
Bi7	0.002	0.3720	0.1400	0.1361	0.0021
Bi8	0.001	0.3678	0.1262	0.1345	0.0056
Bi9	0.003	0.6232	0.1376	0.1180	0.0042
Bi10	0.001	0.6431	0.1363	0.1287	0.0032
Bi11	0.001	0.3824	0.3863	0.1213	0.0198
Bi12	0.003	-0.3800	-0.3881	-0.1201	0.0421

Table S4 The cation-oxygen bond lengths in the $Na_{0.625}Ca_{8.668}Al_6O_{18}$:0.02$Bi^{3+}$

	Atom	Average		Atom	Average	
Six-coordination	**Ca1**			**Ca4/ Na2**		
	O11	2.3121×3	**2.3232**	O6	2.3543×3	**2.3651**
	O12	2.3342×3		O8	2.3759×3	
	Ca2					
	O9	2.3474×3	**2.3543**			
	O10	2.3612×3				
					Total average:2.3511	
Seven-coordination	**Ca11**			**Ca12**		
	O7	2.2542		O8	2.2822	
	O11	2.2752		O12	2.3304	
	O5	2.3692	**2.5129**	O6	2.3332	**2.5110**
	O3	2.4712		O11	2.5820×2	
	O12	2.5929×2		O4	2.7312	
	O2	3.0349		O1	2.7962	
					Total average:2.5110	
Eight-coordination	**Ca7**			**Ca9**		
	O9	2.2109		O10	2.2972	
	O3	2.325	**2.6396**	O4	2.2977	**2.6450**
	O5	2.5892		O6	2.3793	

	O5	2.6065		O2	2.4884	
	O1	2.6321		O9	2.6497	
	O4	2.7623		O8	2.8873	
	O10	2.9656		O3	2.991	
	O7	3.0249		O6	3.1693	
	Ca8			**Ca10**		
	O9	2.2625		O10	2.3567	
	O3	2.3861		O6	2.3584	
	O5	2.5425		O2	2.3748	
	O4	2.5562	**2.6384**	O4	2.4391	**2.6433**
	O1	2.5647		O8	2.6661	
	O5	2.7394		O6	2.8291	
	O10	2.8302		O9	2.9946	
	O7	3.2257		O3	3.1274	
					Total average:2.6416	
Nine-coordination	**Ca5/ Na3**			**Ca6/ Na4**		
	O7	2.5029×3		O1	2.5904×3	
	O10	2.6584×3	**2.7427**	O8	2.6707×3	**2.6939**
	O2	2.8000×3		O9	2.8205×3	
					Total average:2.7183	

Table S5 The lattice, site occupation and isotropic displacement parameters of $Na_2Ca_{7.98}Al_6O_{18}$:0.02Bi^{3+}

Atom	Occup.	*x*	*y*	*z*	Uiso
Ca1	0.500	0.0009	0.0021	0.5196	0.148
Ca2	1.000	0.0008	0.0185	0.2382	0.0215
Ca3	1.000	0.0119	0.2677	0.1325	0.0474
Ca4	1.000	0.2625	0.2702	0.2523	0.0041
Ca5	0.678	0.2610	0.2460	0.4989	0.0467
Na1	0.322	0.2610	0.2460	0.4989	0.0014
Ca6	0.500	0.5024	0.4979	0.4838	0.0025
Ca7	1.000	0.4916	0.4833	0.2402	0.0057
Ca8	1.000	0.5055	0.2329	-0.1341	0.0145
Ca9	1.000	0.7494	0.2297	-0.2533	0.0149
Ca10	0.322	0.7629	0.2524	-0.4986	0.0027
Na2	0.678	0.7629	0.2524	-0.4986	0.0027
Na3	0.500	0.001	-0.0150	-0.0099	0.0375
Na4	0.500	0.5023	0.5184	0.0110	0.0245
Al1	1.000	-0.0027	-0.2155	0.1164	0.0024
Al2	1.000	0.2403	-0.0041	0.1143	0.0467
Al3	1.000	0.2395	0.0058	-0.1074	0.0069
Al4	1.000	0.4944	0.7137	-0.1161	0.0103
Al5	1.000	0.7351	0.5030	-0.1113	0.0034

Al6	1.000	0.7442	0.4950	0.1099	0.0097
O1	1.000	-0.1380	-0.1309	0.1070	0.0238
O2	1.000	0.1172	-0.1079	0.1287	0.0229
O3	1.000	0.2864	-0.0223	0.0026	0.0141
O4	1.000	-0.0150	-0.2877	0.2174	0.0196
O5	1.000	0.0235	-0.2941	0.0174	0.0136
O6	1.000	0.3611	-0.0703	0.1727	0.0163
O7	1.000	0.1849	0.1433	0.1367	0.0195
O8	1.000	0.1617	-0.1295	-0.1379	0.0158
O9	1.000	0.3680	0.0677	-0.1604	0.0145
O10	1.000	0.3522	0.6365	-0.1118	0.0180
O11	1.000	0.6053	0.5968	-0.1242	0.0219
O12	1.000	0.7853	0.5221	-0.0013	0.0160
O13	1.000	0.4990	0.7844	-0.2184	0.0067
O14	1.000	0.5142	0.7929	-0.0173	0.0079
O15	1.000	0.8508	0.5733	-0.1727	0.0078
O16	1.000	0.6888	0.3503	-0.1297	0.0027
O17	1.000	0.6638	0.6255	0.1450	0.0114
O18	1.000	0.8760	0.4337	0.1591	0.0124
Bi1	0.001	0.0009	0.0021	0.5196	0.0054
Bi2	0.003	0.0008	0.0185	0.2382	0.0412
Bi3	0.001	0.0119	0.2677	0.1325	0.0456
Bi4	0.002	0.2625	0.2702	0.2523	0.0035
Bi5	0.001	0.2610	0.2460	0.4989	0.0157
Bi6	0.004	0.5024	0.4979	0.4838	0.0168
Bi7	0.002	0.4916	0.4833	0.2402	0.0031
Bi8	0.001	0.5055	0.2329	-0.1341	0.0024
Bi9	0.001	0.7494	0.2297	-0.2533	0.0261
Bi10	0.004	0.7629	0.2524	-0.4986	0.0010

Table S6 The cation-oxygen bond lengths in the $Na_2Ca_{7.98}Al_6O_{18}$:0.02Bi^{3+}

	Atom	**Length**	**Average**	**Atom**	**Length**	**Average**
Six-coordination	**Ca3**			**Ca8**		
	O7	2.3169		O13	2.3019	
	O5	2.319		O14	2.3184	
	O4	2.3502	**2.3543**	O6	2.3583	**2.3531**
	O15	2.3619		O16	2.3671	
	O18	2.3651		O9	2.3686	
	O8	2.4129		O17	2.4042	
					Total average:2.3537	
Seven-coordination	**Ca1**			**Ca6**		
	O5	2.2842×2		O14	2.2818×2	
	O12	2.3665×2	**2.5631**	O3	2.3491×2	**2.5701**
	O18	2.6056		O9	2.7216	

	O15	2.9272		O6	2.8918	
	O18	3.1079		O9	3.1153	
	Ca2			**Ca7**		
	O4	2.2136		O6	2.1551	
	O18	2.2492		O13	2.2503	
	O15	2.3395		O9	2.3312	
	O2	2.4964	**2.5373**	O11	2.4758	**2.5401**
	O8	2.623		O17	2.5155	
	O7	2.8644		O10	2.9733	
	O1	2.9752		O16	3.0792	
					Total average:2.5527	
Eight-coordination	**Ca4**			**Ca5/Na1**		
	O17	2.3506		O1	2.4787	
	O7	2.3813		O12	2.4821	
	O15	2.4198		O14	2.5131	
	O9	2.4816	**2.6875**	O7	2.5453	**2.6553**
	O13	2.7100		O17	2.6689	
	O1	2.7424		O11	2.8868	
	O4	2.8022		O3	3.0122	
	O11	2.8126		O5	3.1347	
	Ca9			**Ca10/Na2**		
	O16	2.3764		O5	2.3945	
	O6	2.4343		O16	2.4144	
	O8	2.4458		O10	2.4376	
	O10	2.5324	**2.6155**	O3	2.5042	**2.6460**
	O18	2.6076		O8	2.5659	
	O2	2.722		O2	2.8066	
	O13	2.7993		O12	2.9896	
	O4	3.0062		O14	3.0554	
					Total average:2.6261	

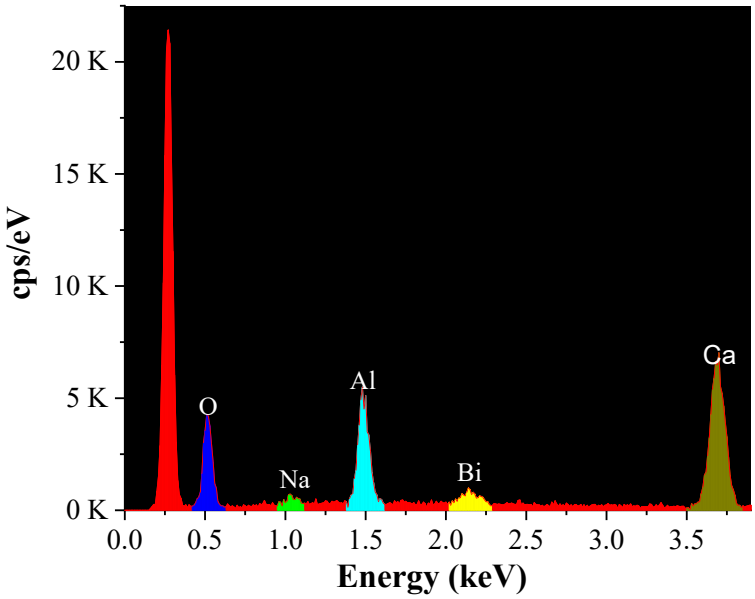

Figure S5 EDS analysis results of $Na_{0.625}Ca_{8.668}Al_6O_{18}$: $0.02Bi^{3+}$.

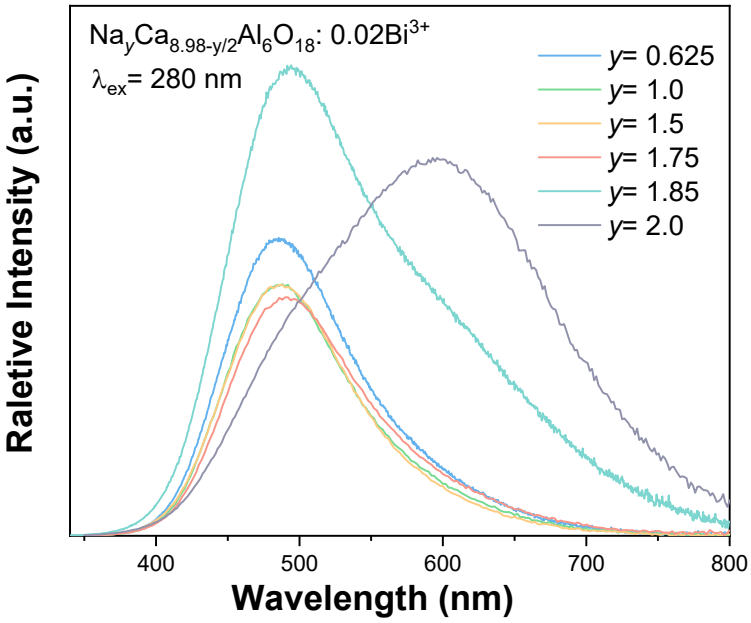

Figure S6 The PL emission spectra of $Na_yCa_{9-y/2}Al_6O_{18}$: $0.02Bi^{3+}$ ($0.625 \leq y \leq 2$).

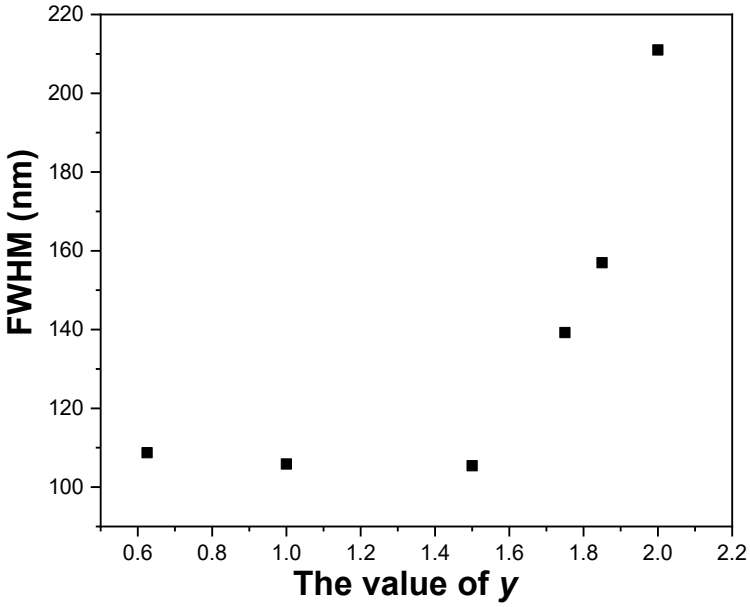

Figure S7 FWHM values of $Na_yCa_{8.98-y/2}Al_6O_{18}$: $0.02Bi^{3+}$ ($0.625 \le y \le 2$) upon 280 nm excitation.

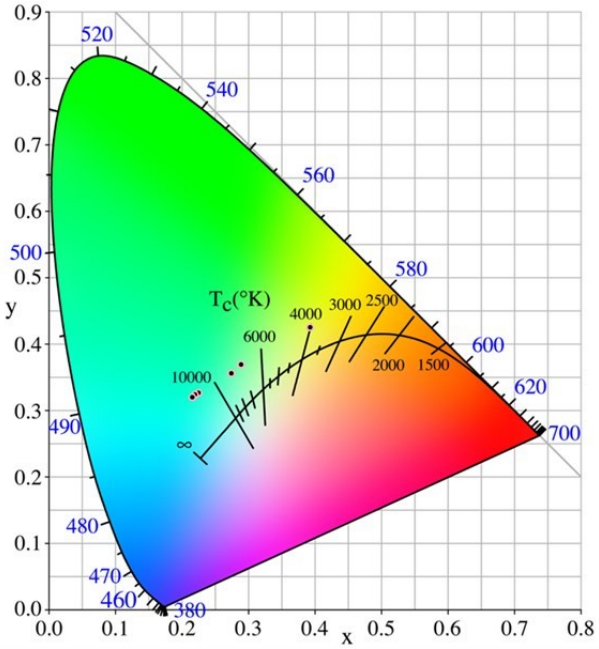

Figure S8 CIE coordinates of $Na_yCa_{8.98-y/2}Al_6O_{18}$: $0.02Bi^{3+}$ ($0.625 \le y \le 2$) upon 280 nm excitation.

Table S7 CIE coordinates of $Na_yCa_{8.98-y/2}Al_6O_{18}$: $0.02Bi^{3+}$ ($0.625 \le y \le 2$).

y (Na)	CIE *x*	CIE *y*	CCT/K
0.625	0.2258	0.3265	13220
1	0.2195	0.3236	14138
1.5	0.2101	0.3199	15632
1.75	0.2748	0.3564	8283
1.85	0.2893	0.3697	7351
2	0.3931	0.425	3986

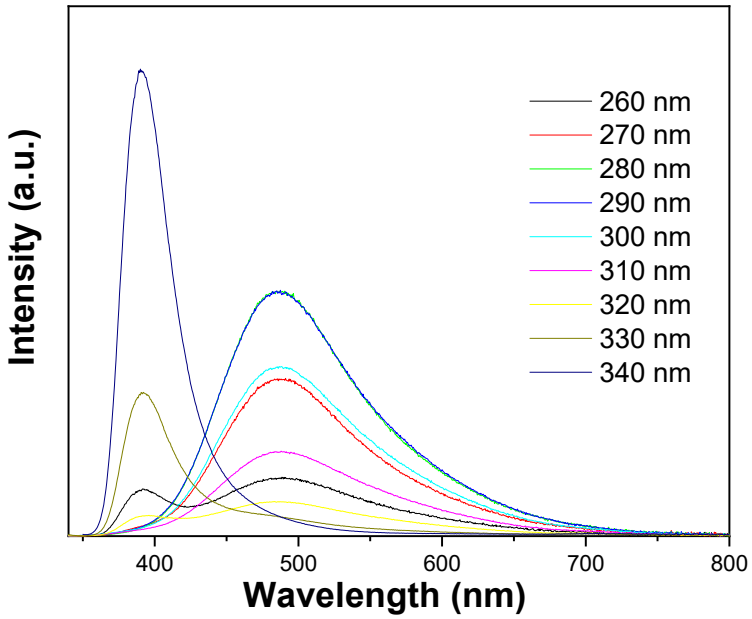

Figure S9 Emission spectra of $Na_{0.625}Ca_{8.683}Al_6O_{18}$: $0.005Bi^{3+}$ upon different wavelength excitation.

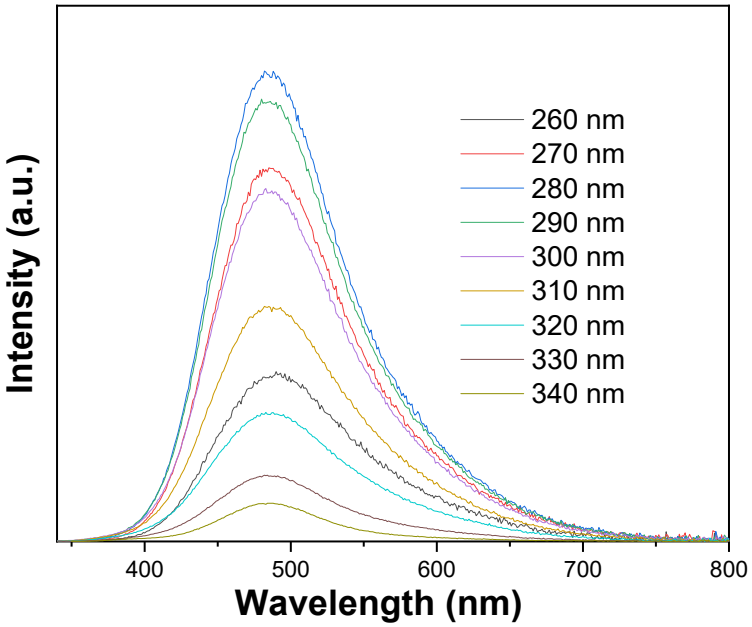

Figure S10 Emission spectra of $Na_{0.625}Ca_{8.668}Al_6O_{18}$: $0.02Bi^{3+}$ upon different wavelength excitation.

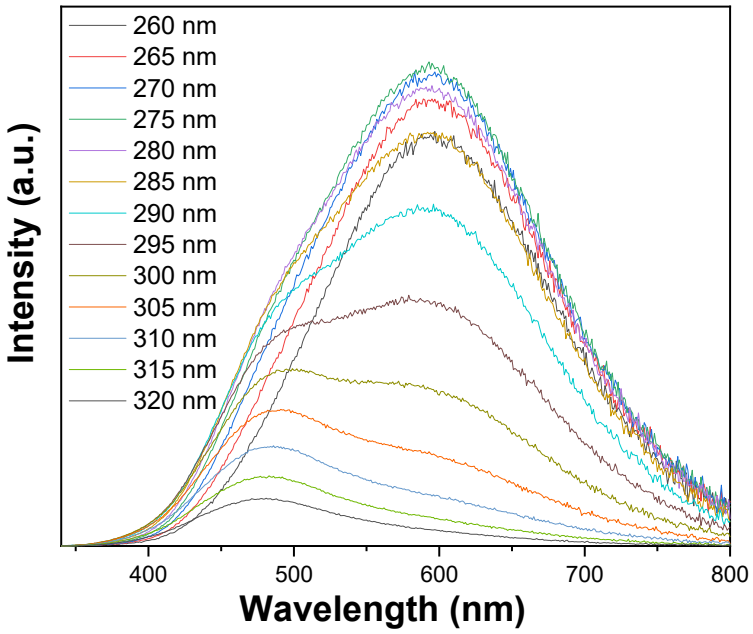

Figure S11 Emission spectra of $Na_2Ca_{7.98}Al_6O_{18}$:0.02Bi^{3+} upon different wavelength excitation.

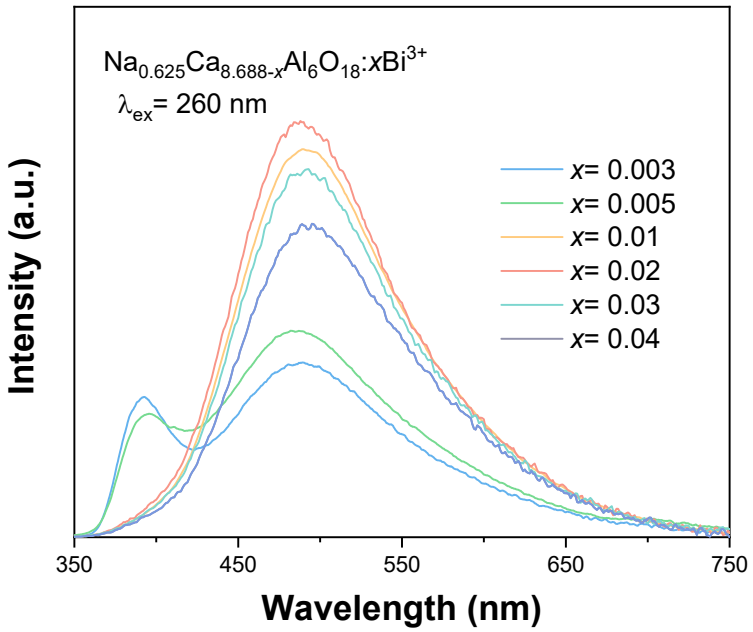

Figure S12 PL (λ_{ex}= 260 nm) spectra of $Na_{0.625}Ca_{8.688-x}Al_6O_{18}$:$x$$Bi^{3+}$ ($0.003 \leq x \leq 0.04$) sample.

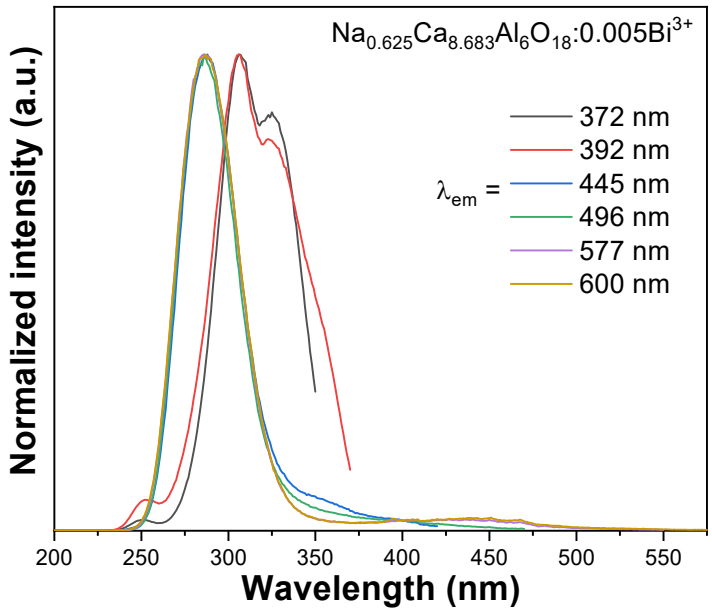

Figure S13 The excitation spectra of $Na_{0.625}Ca_{8.683}Al_6O_{18}$: $0.005Bi^{3+}$ by monitored different wavelength emission.

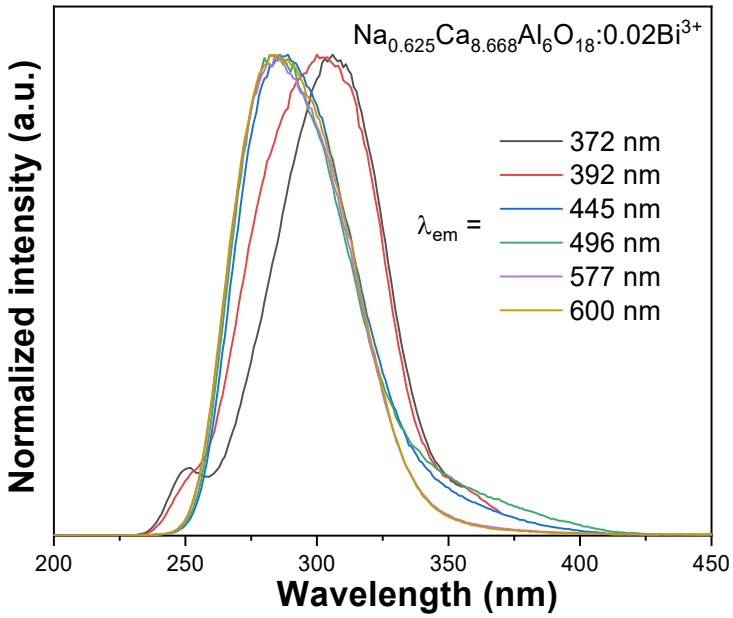

Figure S14 The excitation spectra of $Na_{0.625}Ca_{8.668}Al_6O_{18}$: $0.02Bi^{3+}$ by monitored different

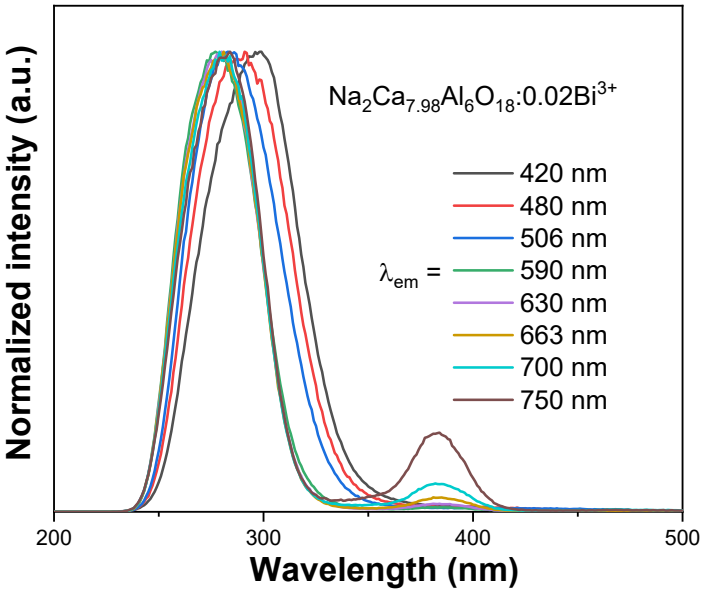

Figure S15 The excitation spectra of $Na_2Ca_{7.98}Al_6O_{18}$: $0.02Bi^{3+}$ by monitored different wavelength emission.

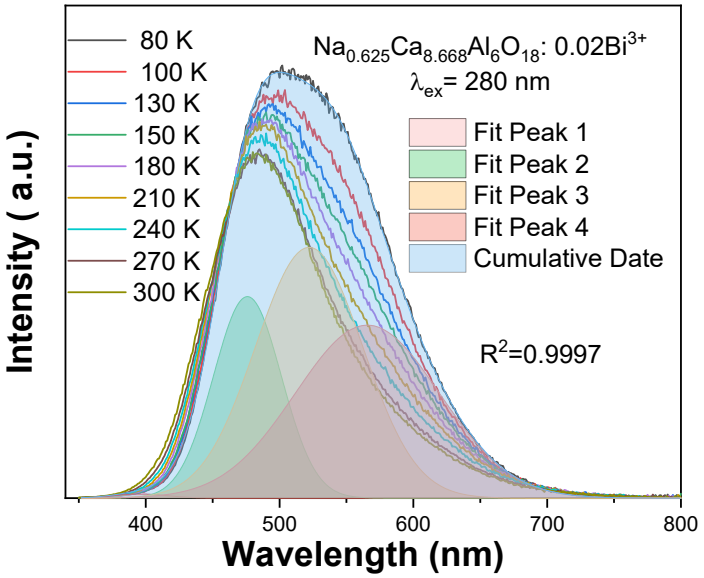

Figure S16 The temperature dependent emission spectra of $Na_{0.625}Ca_{8.668}Al_6O_{18}$:$0.02Bi^{3+}$ ranging from 80 to 300 K;

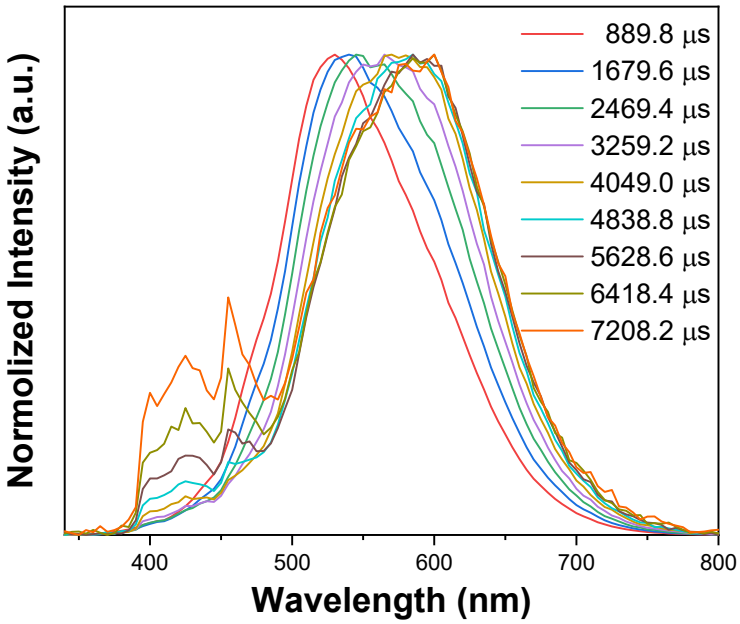

Figure S17 The normalized time-resolved photoluminescence (TRPL) spectra of $Na_2Ca_{7.98}Al_6O_{18}:0.02Bi^{3+}$ at 10 K.

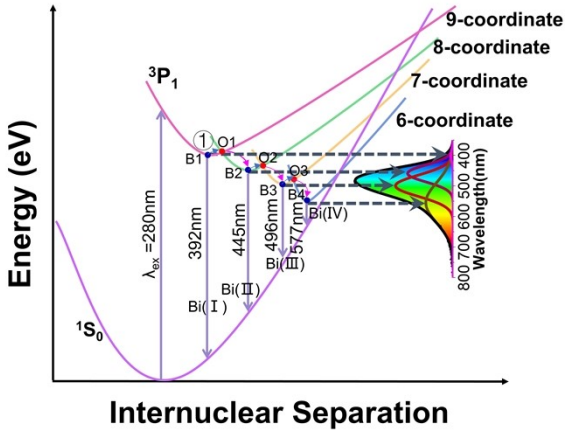

Figure S18 Configurational coordinate diagram of the ground state and four split excited states of $Na_{0.625}Ca_{8.668}Al_6O_{18}:0.02Bi^{3+}$

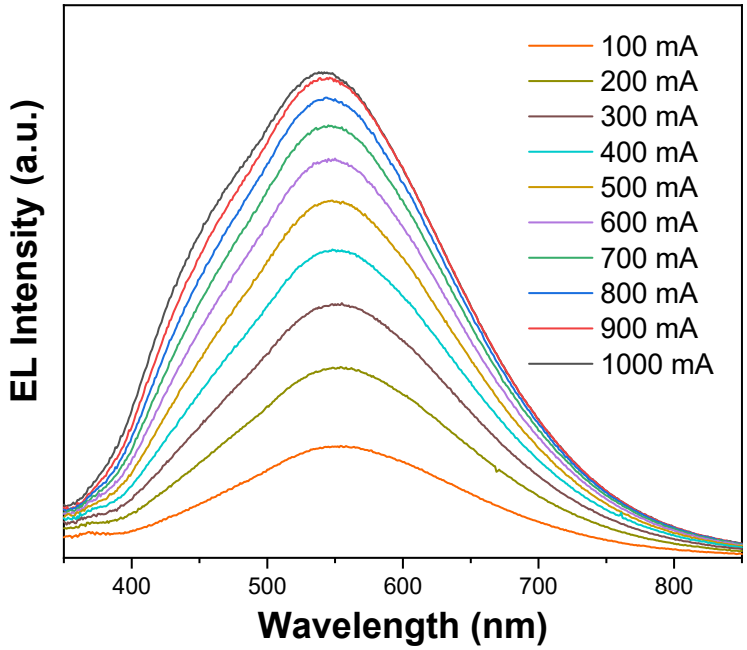

Figure S19 Electroluminescence spectra of the fabricated WLEDs driven by different currents.

Table S8 The CIE coordinates of the fabricated WLEDs driven by different currents.

current (mA)	CIE *x*	CIE *y*	CCT/K
100	0.3574	0.4087	4802
200	0.3559	0.4061	4833
300	0.3533	0.4034	4900
400	0.3503	0.4009	4976
500	0.3468	0.3982	5073
600	0.3440	0.3957	5152
700	0.3412	0.3931	5236
800	0.3382	0.3902	5325
900	0.3354	0.3869	5415
1000	0.3306	0.3809	5577

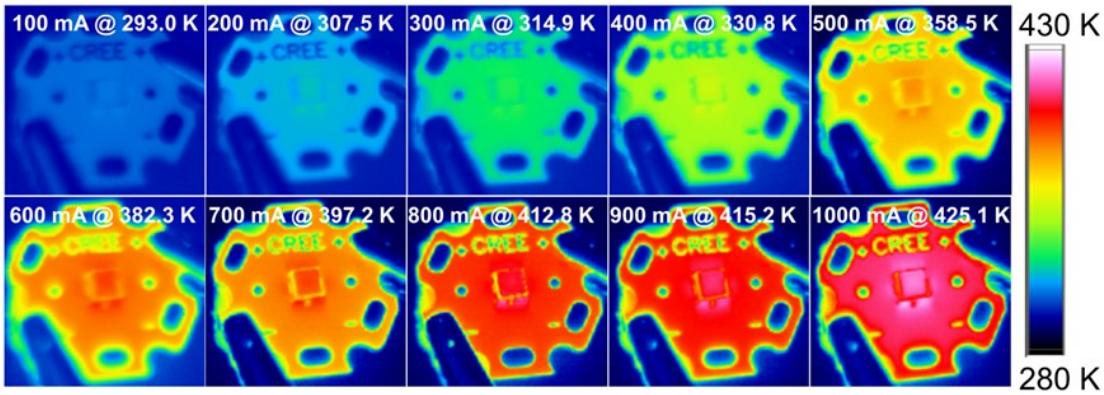

Figure S20 Thermal imaging of the WLED driven at different currents

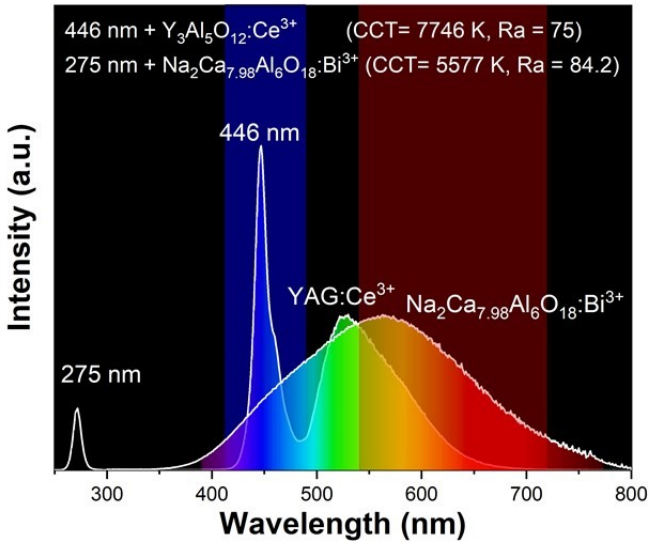

Figure S21 The spectra of 446 nm chip with YAG:Ce^{3+} and 275 nm chip with $Na_2Ca_{7.98}Al_6O_{18}:0.02Bi^{3+}$

Table S9 Comparison of performance parameters of fabricated pc-WLED with other tunable broadband emitting phosphors.

Samples	λ_{ex}(nm)	λ_{em}(nm)	FWHM(nm)	CCT (K)	CIE	R_a	Ref.
$Sr_3Ga_4O_9:Bi^{3+}$	330	530	~200	5896	(0.320,0.466)	79	S1
$Ca_3Ga_4O_9:Bi^{3+}$	370	510	~120	8085	(0.250,0.420)	50.5	S2
$Ba_3Y_4O_9:Bi^{3+}$	350	610	~150	3720	(0.476,0.445)	95	S3
$Ba_3Y_2Lu_2O_9:Bi^{3+}$	350	580	~180	4808	(0.447,0.479)	94	S3
$Ba_2ZnGe_2O_7:Bi^{3+}$	395	500, 620	-	3942	(0.369,0.311)	84.6	S4
$Ba_2MgGe_2O_7:Bi^{3+}$	395	500, 620	-	4466	(0.343,0.301)	98.9	S4
$Na_2Ca_3Nb_2O_9:Bi^{3+}$	365	600	~150	3748	(0.410,0.420)	88.6	S5
CSMKPO:0.02Eu^{2+}	330	490	~175	5186	(0.340,0.346)	89	S6
$YTaO_4$:0.03Bi^{3+}	365	500	~225	9449	(0.274,0.323)	77.8	S7
GAGO:0.06Ce^{3+}	460	575	~150	3778	(0.390,0.380)	73	S8
$Ba_2Y(SiO_4)_3F:Eu$	350	600	~200 nm	3530	(0.402,0.371)	83.5	S9
$Ca_{9.75}Mg_{0.75}(PO_4)_7:Eu^{2+}$	365	575	-	3788	(0.385,0.365)	85	S10
$NaLi_3Si_{0.75}O_4:Eu^{2+}$	365	585	-	6599	(0.312,0.322)	82.9	S11
$BaSrMg(PO_4)_2:Eu^{2+}$	385	460, 550	-	5892	(0.320,0.330)	84	S12
$Na_2Ca_{7.98}Al_6O_{18}:0.02Bi^{3+}$	280	590	228 nm	5577	(0.331,0.381)	84.2	This work

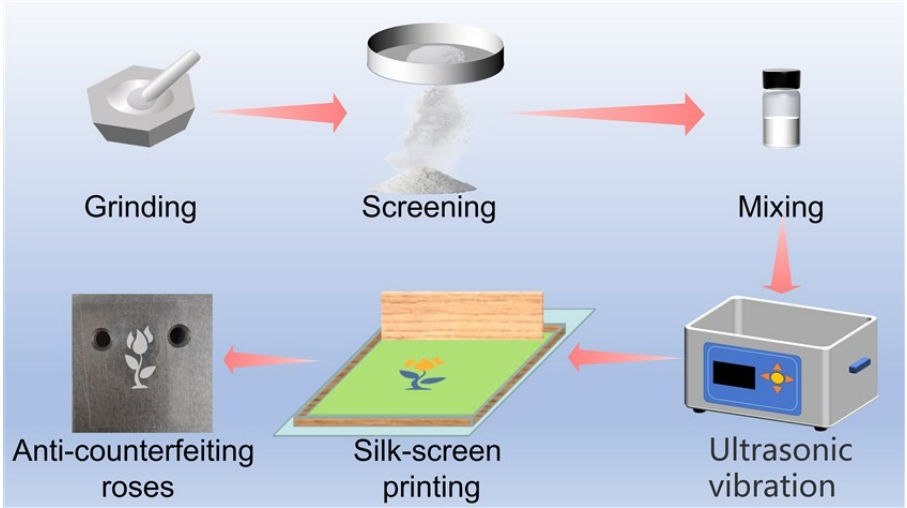

Figure S22 The synthesis process of the fabricated anti-counterfeiting rose label

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