Supporting Information

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

Qingfeng Bian, Ge Zhu*, Zhuowei Li, Shanshan Li, Wen Xu, Yan Cong, Ming He, Shuangyu Xin, Bin Dong*
Figure S1 XRD patterns for \( \text{Na}_{0.625}\text{Ca}_{8.688-x}\text{Al}_6\text{O}_{18}: x\text{Bi}^{3+} \) (0.003 \( \leq x \leq 0.04 \)) with different \( \text{Bi}^{3+} \) doing. contents

\[
x = 0.04 \\
x = 0.03 \\
x = 0.02 \\
x = 0.01 \\
x = 0.005 \\
x = 0.003 \\
\]

Figure S2 XRD patterns for \( \text{Na}_y\text{Ca}_{8.98-y/2}\text{Al}_6\text{O}_{18}: 0.02\text{Bi}^{3+} \) (0.625 \( \leq y \leq 2 \)).
Figure S3 X-ray diffraction Rietveld refinement of the Na$_{0.625}$Ca$_{8.668}$Al$_6$O$_{18}$:0.02Bi$^{3+}$

Figure S4 X-ray diffraction Rietveld refinement of the Na$_2$Ca$_{7.98}$Al$_6$O$_{18}$:0.02Bi$^{3+}$

Table S1 The crystallographic parameters of Na$_{0.625}$Ca$_{8.668}$Al$_6$O$_{18}$:0.02Bi$^{3+}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_13$</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td>$a=b=c=15.236$ Å [\alpha=\beta=\gamma=90^\circ]</td>
</tr>
<tr>
<td>Unit cell volume</td>
<td>$V=3536.82$ Å</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>2.36</td>
</tr>
<tr>
<td>$R_p$</td>
<td>7.21 %</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>10.01 %</td>
</tr>
</tbody>
</table>
Table S2 The crystallographic parameters of Na$_2$Ca$_{7.98}$Al$_6$O$_{18}$:0.02Bi$^{3+}$

<table>
<thead>
<tr>
<th></th>
<th>Na$<em>2$Ca$</em>{7.98}$Al$<em>6$O$</em>{18}$:0.02Bi$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td>$a=10.874$ Å, $b=10.849$ Å, $c=15.130$ Å, $\alpha=\beta=\gamma=90^\circ$</td>
</tr>
<tr>
<td>Unit cell volume</td>
<td>$V=1784.92$ Å</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>2.63</td>
</tr>
<tr>
<td>$R_P$</td>
<td>8.63 %</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>11.29 %</td>
</tr>
</tbody>
</table>

Table S3 The lattice, site occupation and isotropic displacement parameters of Na$_{0.625}$Ca$_{8.668}$Al$_6$O$_{18}$:0.02Bi$^{3+}$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Occup.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1</td>
<td>0.9982</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0015</td>
</tr>
<tr>
<td>Ca2</td>
<td>0.9979</td>
<td>0.5018</td>
<td>0.5018</td>
<td>0.5018</td>
<td>0.0021</td>
</tr>
<tr>
<td>Ca3</td>
<td>0.9080</td>
<td>0.2630</td>
<td>0.2630</td>
<td>0.2630</td>
<td>0.0041</td>
</tr>
<tr>
<td>Na1</td>
<td>0.090</td>
<td>0.2630</td>
<td>0.2630</td>
<td>0.2630</td>
<td>0.0044</td>
</tr>
<tr>
<td>Ca4</td>
<td>0.729</td>
<td>-0.2562</td>
<td>-0.2562</td>
<td>-0.2562</td>
<td>0.0072</td>
</tr>
<tr>
<td>Na2</td>
<td>0.270</td>
<td>-0.2562</td>
<td>-0.2562</td>
<td>-0.2562</td>
<td>0.0081</td>
</tr>
<tr>
<td>Ca5</td>
<td>0.966</td>
<td>0.3814</td>
<td>0.3814</td>
<td>0.3814</td>
<td>0.0041</td>
</tr>
<tr>
<td>Na3</td>
<td>0.030</td>
<td>0.3814</td>
<td>0.3814</td>
<td>0.3814</td>
<td>0.0157</td>
</tr>
<tr>
<td>Ca6</td>
<td>0.759</td>
<td>-0.3763</td>
<td>-0.3763</td>
<td>-0.3763</td>
<td>0.0041</td>
</tr>
<tr>
<td>Na4</td>
<td>0.240</td>
<td>-0.3763</td>
<td>-0.3763</td>
<td>-0.3763</td>
<td>0.0012</td>
</tr>
<tr>
<td>Ca7</td>
<td>0.498</td>
<td>0.3720</td>
<td>0.1400</td>
<td>0.1361</td>
<td>0.0344</td>
</tr>
<tr>
<td>Ca8</td>
<td>0.499</td>
<td>0.3678</td>
<td>0.1262</td>
<td>0.1345</td>
<td>0.0421</td>
</tr>
<tr>
<td>Ca9</td>
<td>0.497</td>
<td>0.6232</td>
<td>0.1376</td>
<td>0.1180</td>
<td>0.0013</td>
</tr>
<tr>
<td>Ca10</td>
<td>0.499</td>
<td>0.6431</td>
<td>0.1363</td>
<td>0.1287</td>
<td>0.0016</td>
</tr>
<tr>
<td>Ca11</td>
<td>0.998</td>
<td>0.3824</td>
<td>0.3863</td>
<td>0.1213</td>
<td>0.0032</td>
</tr>
<tr>
<td>Ca12</td>
<td>0.997</td>
<td>-0.3800</td>
<td>-0.3881</td>
<td>-0.1201</td>
<td>0.0057</td>
</tr>
<tr>
<td>Na5</td>
<td>0.310</td>
<td>0.1210</td>
<td>0.1210</td>
<td>0.1210</td>
<td>0.0247</td>
</tr>
<tr>
<td>Na6</td>
<td>0.310</td>
<td>0.8750</td>
<td>0.8750</td>
<td>0.8750</td>
<td>0.0024</td>
</tr>
<tr>
<td>Al1</td>
<td>1.000</td>
<td>0.2539</td>
<td>0.0134</td>
<td>0.0167</td>
<td>0.0058</td>
</tr>
<tr>
<td>Al2</td>
<td>1.000</td>
<td>-0.2534</td>
<td>-0.0129</td>
<td>-0.0232</td>
<td>0.0048</td>
</tr>
<tr>
<td>Al3</td>
<td>1.000</td>
<td>0.2434</td>
<td>0.2371</td>
<td>0.0053</td>
<td>0.0068</td>
</tr>
<tr>
<td>Al4</td>
<td>1.000</td>
<td>-0.2445</td>
<td>-0.2377</td>
<td>-0.0063</td>
<td>0.0055</td>
</tr>
<tr>
<td>O1</td>
<td>1.000</td>
<td>0.2630</td>
<td>0.1264</td>
<td>0.0029</td>
<td>0.0236</td>
</tr>
<tr>
<td>O2</td>
<td>1.000</td>
<td>-0.2658</td>
<td>-0.1258</td>
<td>-0.0230</td>
<td>0.0369</td>
</tr>
<tr>
<td>Atom</td>
<td>Average</td>
<td>Atom</td>
<td>Average</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>---------</td>
<td>-------</td>
<td>---------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3</td>
<td>1.000</td>
<td>0.4759</td>
<td>0.1327</td>
<td>0.2475</td>
<td>0.0113</td>
</tr>
<tr>
<td>O4</td>
<td>1.000</td>
<td>-0.4952</td>
<td>-0.1310</td>
<td>-0.2368</td>
<td>0.0195</td>
</tr>
<tr>
<td>O5</td>
<td>1.000</td>
<td>0.2729</td>
<td>0.2765</td>
<td>0.1082</td>
<td>0.0175</td>
</tr>
<tr>
<td>O6</td>
<td>1.000</td>
<td>-0.2629</td>
<td>-0.2906</td>
<td>-0.1058</td>
<td>0.0187</td>
</tr>
<tr>
<td>O7</td>
<td>1.000</td>
<td>0.2406</td>
<td>0.4114</td>
<td>0.3040</td>
<td>0.0160</td>
</tr>
<tr>
<td>O8</td>
<td>1.000</td>
<td>-0.2281</td>
<td>-0.4062</td>
<td>-0.2878</td>
<td>0.0156</td>
</tr>
<tr>
<td>O9</td>
<td>1.000</td>
<td>0.3502</td>
<td>-0.0321</td>
<td>-0.2878</td>
<td>0.0138</td>
</tr>
<tr>
<td>O10</td>
<td>1.000</td>
<td>-0.3505</td>
<td>0.0233</td>
<td>0.0234</td>
<td>0.0199</td>
</tr>
<tr>
<td>O11</td>
<td>1.000</td>
<td>0.1497</td>
<td>-0.0713</td>
<td>-0.0171</td>
<td>0.0129</td>
</tr>
<tr>
<td>O12</td>
<td>1.000</td>
<td>-0.1515</td>
<td>0.0150</td>
<td>0.0163</td>
<td>0.0075</td>
</tr>
<tr>
<td>Bi1</td>
<td>0.002</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0009</td>
</tr>
<tr>
<td>Bi2</td>
<td>0.002</td>
<td>0.5018</td>
<td>0.5018</td>
<td>0.5018</td>
<td>0.0011</td>
</tr>
<tr>
<td>Bi3</td>
<td>0.002</td>
<td>0.2630</td>
<td>0.2630</td>
<td>0.2630</td>
<td>0.0031</td>
</tr>
<tr>
<td>Bi4</td>
<td>0.001</td>
<td>-0.2562</td>
<td>-0.2562</td>
<td>-0.2562</td>
<td>0.0023</td>
</tr>
<tr>
<td>Bi5</td>
<td>0.001</td>
<td>0.3814</td>
<td>0.3814</td>
<td>0.3814</td>
<td>0.0025</td>
</tr>
<tr>
<td>Bi6</td>
<td>0.001</td>
<td>-0.3763</td>
<td>-0.3763</td>
<td>-0.3763</td>
<td>0.0032</td>
</tr>
<tr>
<td>Bi7</td>
<td>0.002</td>
<td>0.3720</td>
<td>0.1400</td>
<td>0.1361</td>
<td>0.0021</td>
</tr>
<tr>
<td>Bi8</td>
<td>0.001</td>
<td>0.3678</td>
<td>0.1262</td>
<td>0.1345</td>
<td>0.0056</td>
</tr>
<tr>
<td>Bi9</td>
<td>0.003</td>
<td>0.6232</td>
<td>0.1376</td>
<td>0.1180</td>
<td>0.0042</td>
</tr>
<tr>
<td>Bi10</td>
<td>0.001</td>
<td>0.6431</td>
<td>0.1363</td>
<td>0.1287</td>
<td>0.0032</td>
</tr>
<tr>
<td>Bi11</td>
<td>0.001</td>
<td>0.3824</td>
<td>0.3863</td>
<td>0.1213</td>
<td>0.0198</td>
</tr>
<tr>
<td>Bi12</td>
<td>0.003</td>
<td>-0.3800</td>
<td>-0.3881</td>
<td>-0.1201</td>
<td>0.0421</td>
</tr>
</tbody>
</table>

Table S4 The cation-oxygen bond lengths in the Na$_{0.625}$Ca$_{8.668}$Al$_{6}$O$_{18}$·0.02Bi$_{3}^+$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Average</th>
<th>Atom</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Six-</td>
<td>Ca1</td>
<td>Ca4/Na2</td>
<td></td>
</tr>
<tr>
<td>coordination</td>
<td>O11</td>
<td>2.3121×3</td>
<td>O6</td>
</tr>
<tr>
<td></td>
<td>O12</td>
<td>2.3342×3</td>
<td>O8</td>
</tr>
<tr>
<td></td>
<td>Ca2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O9</td>
<td>2.3474×3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O10</td>
<td>2.3612×3</td>
<td></td>
</tr>
<tr>
<td>Seven-coordination</td>
<td>O7</td>
<td>2.2542</td>
<td>O8</td>
</tr>
<tr>
<td></td>
<td>O11</td>
<td>2.2752</td>
<td>O12</td>
</tr>
<tr>
<td></td>
<td>O5</td>
<td>2.3692</td>
<td>O6</td>
</tr>
<tr>
<td></td>
<td>O3</td>
<td>2.4712</td>
<td>O11</td>
</tr>
<tr>
<td></td>
<td>O12</td>
<td>2.5929×2</td>
<td>O4</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>3.0349</td>
<td>O1</td>
</tr>
<tr>
<td>Total average:2.3511</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Eight-coordination | Ca7 | 2.2109 | O10 | 2.2972 |
|                    | O3  | 2.325  | O4  | 2.2977 |
|                    | O5  | 2.5892 | O6  | 2.3793 |
| Total average:2.6450 |
Table S5 The lattice, site occupation and isotropic displacement parameters of Na$_2$Ca$_{7.98}$Al$_6$O$_{18}$:0.02Bi$^{3+}$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Occup.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1</td>
<td>0.500</td>
<td>0.0009</td>
<td>0.0021</td>
<td>0.5196</td>
<td>0.148</td>
</tr>
<tr>
<td>Ca2</td>
<td>1.000</td>
<td>0.0008</td>
<td>0.0185</td>
<td>0.2382</td>
<td>0.0215</td>
</tr>
<tr>
<td>Ca3</td>
<td>1.000</td>
<td>0.0119</td>
<td>0.2677</td>
<td>0.1325</td>
<td>0.0474</td>
</tr>
<tr>
<td>Ca4</td>
<td>1.000</td>
<td>0.2625</td>
<td>0.2702</td>
<td>0.2523</td>
<td>0.0041</td>
</tr>
<tr>
<td>Ca5</td>
<td>0.678</td>
<td>0.2610</td>
<td>0.2460</td>
<td>0.4989</td>
<td>0.0467</td>
</tr>
<tr>
<td>Na1</td>
<td>0.322</td>
<td>0.2610</td>
<td>0.2460</td>
<td>0.4989</td>
<td>0.0014</td>
</tr>
<tr>
<td>Ca6</td>
<td>0.500</td>
<td>0.5024</td>
<td>0.4979</td>
<td>0.4838</td>
<td>0.0025</td>
</tr>
<tr>
<td>Ca7</td>
<td>1.000</td>
<td>0.4916</td>
<td>0.4833</td>
<td>0.2402</td>
<td>0.0057</td>
</tr>
<tr>
<td>Ca8</td>
<td>1.000</td>
<td>0.5055</td>
<td>0.2329</td>
<td>-0.1341</td>
<td>0.0145</td>
</tr>
<tr>
<td>Ca9</td>
<td>1.000</td>
<td>0.7494</td>
<td>0.2297</td>
<td>-0.2533</td>
<td>0.0149</td>
</tr>
<tr>
<td>Ca10</td>
<td>0.322</td>
<td>0.7629</td>
<td>0.2524</td>
<td>-0.4986</td>
<td>0.0027</td>
</tr>
<tr>
<td>Na2</td>
<td>0.678</td>
<td>0.7629</td>
<td>0.2524</td>
<td>-0.4986</td>
<td>0.0027</td>
</tr>
<tr>
<td>Na3</td>
<td>0.500</td>
<td>0.001</td>
<td>-0.0150</td>
<td>-0.0099</td>
<td>0.0375</td>
</tr>
<tr>
<td>Na4</td>
<td>0.500</td>
<td>0.5023</td>
<td>0.5184</td>
<td>0.0110</td>
<td>0.0245</td>
</tr>
<tr>
<td>Al1</td>
<td>1.000</td>
<td>-0.0027</td>
<td>-0.2155</td>
<td>0.1164</td>
<td>0.0024</td>
</tr>
<tr>
<td>Al2</td>
<td>1.000</td>
<td>0.2403</td>
<td>-0.0041</td>
<td>0.1143</td>
<td>0.0467</td>
</tr>
<tr>
<td>Al3</td>
<td>1.000</td>
<td>0.2395</td>
<td>0.0058</td>
<td>-0.1074</td>
<td>0.0069</td>
</tr>
<tr>
<td>Al4</td>
<td>1.000</td>
<td>0.4944</td>
<td>0.7137</td>
<td>-0.1161</td>
<td>0.0103</td>
</tr>
<tr>
<td>Al5</td>
<td>1.000</td>
<td>0.7351</td>
<td>0.5030</td>
<td>-0.1113</td>
<td>0.0034</td>
</tr>
<tr>
<td></td>
<td>Atom</td>
<td>Length A</td>
<td>Average</td>
<td>Atom</td>
<td>Length B</td>
</tr>
<tr>
<td>----</td>
<td>------</td>
<td>----------</td>
<td>---------</td>
<td>------</td>
<td>----------</td>
</tr>
<tr>
<td></td>
<td>Ca3</td>
<td>2.3169</td>
<td></td>
<td>Ca8</td>
<td>2.3019</td>
</tr>
<tr>
<td></td>
<td>O7</td>
<td>2.319</td>
<td></td>
<td>O13</td>
<td>2.3184</td>
</tr>
<tr>
<td></td>
<td>O5</td>
<td>2.3502</td>
<td></td>
<td>O14</td>
<td>2.3583</td>
</tr>
<tr>
<td></td>
<td>O4</td>
<td>2.3543</td>
<td></td>
<td>O6</td>
<td>2.3531</td>
</tr>
<tr>
<td></td>
<td>O15</td>
<td>2.3619</td>
<td></td>
<td>O16</td>
<td>2.3671</td>
</tr>
<tr>
<td></td>
<td>O18</td>
<td>2.3651</td>
<td></td>
<td>O9</td>
<td>2.3686</td>
</tr>
<tr>
<td></td>
<td>O8</td>
<td>2.4129</td>
<td></td>
<td>O17</td>
<td>2.4042</td>
</tr>
<tr>
<td></td>
<td>Bi1</td>
<td>0.001</td>
<td></td>
<td></td>
<td>0.5196</td>
</tr>
<tr>
<td></td>
<td>Bi2</td>
<td>0.003</td>
<td></td>
<td></td>
<td>0.2382</td>
</tr>
<tr>
<td></td>
<td>Bi3</td>
<td>0.001</td>
<td></td>
<td></td>
<td>0.1325</td>
</tr>
<tr>
<td></td>
<td>Bi4</td>
<td>0.002</td>
<td></td>
<td></td>
<td>0.2523</td>
</tr>
<tr>
<td></td>
<td>Bi5</td>
<td>0.001</td>
<td></td>
<td></td>
<td>0.4989</td>
</tr>
<tr>
<td></td>
<td>Bi6</td>
<td>0.004</td>
<td></td>
<td></td>
<td>0.4838</td>
</tr>
<tr>
<td></td>
<td>Bi7</td>
<td>0.002</td>
<td></td>
<td></td>
<td>0.2402</td>
</tr>
<tr>
<td></td>
<td>Bi8</td>
<td>0.001</td>
<td></td>
<td></td>
<td>0.1341</td>
</tr>
<tr>
<td></td>
<td>Bi9</td>
<td>0.001</td>
<td></td>
<td></td>
<td>0.2533</td>
</tr>
<tr>
<td></td>
<td>Bi10</td>
<td>0.004</td>
<td></td>
<td></td>
<td>0.4986</td>
</tr>
</tbody>
</table>

**Table S6** The cation-oxygen bond lengths in the Na$_2$Ca$_{7.98}$Al$_6$O$_{18}$:0.02Bi$^{3+}$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Length A</th>
<th>Average</th>
<th>Atom</th>
<th>Length B</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1</td>
<td>2.2842×2</td>
<td></td>
<td>Ca6</td>
<td>2.2818×2</td>
<td></td>
</tr>
<tr>
<td>O5</td>
<td>2.3665×2</td>
<td>2.5631</td>
<td>O3</td>
<td>2.3491×2</td>
<td>2.5701</td>
</tr>
<tr>
<td>O12</td>
<td>2.6056</td>
<td></td>
<td>O9</td>
<td>2.7216</td>
<td></td>
</tr>
<tr>
<td>O18</td>
<td>2.429</td>
<td></td>
<td></td>
<td>2.4042</td>
<td></td>
</tr>
</tbody>
</table>

**Total average:** 2.3537
<table>
<thead>
<tr>
<th>Eight-coordination</th>
<th>Ca4</th>
<th>Ca5/Na1</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O17</td>
<td>O1</td>
<td>2.3506</td>
<td>2.4787</td>
</tr>
<tr>
<td></td>
<td>O7</td>
<td>O12</td>
<td>2.3813</td>
<td>2.4821</td>
</tr>
<tr>
<td></td>
<td>O15</td>
<td>O14</td>
<td>2.4198</td>
<td>2.5131</td>
</tr>
<tr>
<td></td>
<td>O9</td>
<td>O7</td>
<td>2.4816</td>
<td>2.5453</td>
</tr>
<tr>
<td></td>
<td>O13</td>
<td>O17</td>
<td>2.7100</td>
<td>2.6689</td>
</tr>
<tr>
<td></td>
<td>O1</td>
<td>O11</td>
<td>2.7424</td>
<td>2.8868</td>
</tr>
<tr>
<td></td>
<td>O4</td>
<td>O3</td>
<td>2.8022</td>
<td>3.0122</td>
</tr>
<tr>
<td></td>
<td>O11</td>
<td>O5</td>
<td>2.8126</td>
<td>3.1347</td>
</tr>
<tr>
<td>Ca9</td>
<td>O16</td>
<td>O5</td>
<td>2.3764</td>
<td>2.3945</td>
</tr>
<tr>
<td></td>
<td>O6</td>
<td>O16</td>
<td>2.4343</td>
<td>2.4144</td>
</tr>
<tr>
<td></td>
<td>O8</td>
<td>O10</td>
<td>2.4458</td>
<td>2.4376</td>
</tr>
<tr>
<td></td>
<td>O10</td>
<td>O3</td>
<td>2.5324</td>
<td>2.5042</td>
</tr>
<tr>
<td></td>
<td>O18</td>
<td>O8</td>
<td>2.6076</td>
<td>2.5659</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>O2</td>
<td>2.722</td>
<td>2.8066</td>
</tr>
<tr>
<td></td>
<td>O13</td>
<td>O12</td>
<td>2.7993</td>
<td>2.9896</td>
</tr>
<tr>
<td></td>
<td>O4</td>
<td>O14</td>
<td>3.0062</td>
<td>3.0554</td>
</tr>
</tbody>
</table>

**Total average:** 2.5527

<table>
<thead>
<tr>
<th>Ca2</th>
<th>Ca7</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O4</td>
<td>O6</td>
<td>2.2136</td>
<td>2.1551</td>
</tr>
<tr>
<td>O18</td>
<td>O13</td>
<td>2.2492</td>
<td>2.2503</td>
</tr>
<tr>
<td>O15</td>
<td>O9</td>
<td>2.3395</td>
<td>2.3312</td>
</tr>
<tr>
<td>O2</td>
<td>O11</td>
<td>2.4964</td>
<td>2.5373</td>
</tr>
<tr>
<td>O8</td>
<td>O17</td>
<td>2.623</td>
<td>2.5401</td>
</tr>
<tr>
<td>O7</td>
<td>O10</td>
<td>2.8644</td>
<td>2.9733</td>
</tr>
<tr>
<td>O1</td>
<td>O16</td>
<td>2.9752</td>
<td>3.0792</td>
</tr>
</tbody>
</table>

**Total average:** 2.6261
Figure S5 EDS analysis results of Na$_{0.625}$Ca$_{8.668}$Al$_6$O$_{18}$: 0.02Bi$^{3+}$.

Figure S6 The PL emission spectra of Na$_y$Ca$_{9-y/2}$Al$_6$O$_{18}$: 0.02Bi$^{3+}$ (0.625 $\leq$ $y$ $\leq$ 2).
Figure S7 FWHM values of Na$_y$Ca$_{8.98-y/2}$Al$_6$O$_{18}$: 0.02Bi$^{3+}$ (0.625 ≤ $y$ ≤ 2) upon 280 nm excitation.

Figure S8 CIE coordinates of Na$_y$Ca$_{8.98-y/2}$Al$_6$O$_{18}$: 0.02Bi$^{3+}$ (0.625 ≤ $y$ ≤ 2) upon 280 nm excitation.

Table S7 CIE coordinates of Na$_y$Ca$_{8.98-y/2}$Al$_6$O$_{18}$: 0.02Bi$^{3+}$ (0.625 ≤ $y$ ≤ 2).

<table>
<thead>
<tr>
<th>$y$ (Na)</th>
<th>CIE x</th>
<th>CIE y</th>
<th>CCT/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.625</td>
<td>0.2258</td>
<td>0.3265</td>
<td>13220</td>
</tr>
<tr>
<td>1</td>
<td>0.2195</td>
<td>0.3236</td>
<td>14138</td>
</tr>
<tr>
<td>1.5</td>
<td>0.2101</td>
<td>0.3199</td>
<td>15632</td>
</tr>
<tr>
<td>1.75</td>
<td>0.2748</td>
<td>0.3564</td>
<td>8283</td>
</tr>
<tr>
<td>1.85</td>
<td>0.2893</td>
<td>0.3697</td>
<td>7351</td>
</tr>
<tr>
<td>2</td>
<td>0.3931</td>
<td>0.425</td>
<td>3986</td>
</tr>
</tbody>
</table>
Figure S9 Emission spectra of Na$_{0.625}$Ca$_{8.683}$Al$_6$O$_{18}$: 0.005Bi$^{3+}$ upon different wavelength excitation.

Figure S10 Emission spectra of Na$_{0.625}$Ca$_{8.668}$Al$_6$O$_{18}$: 0.02Bi$^{3+}$ upon different wavelength excitation.
Figure S11 Emission spectra of Na$_2$Ca$_{7.98}$Al$_{6}$O$_{18}$:0.02Bi$^{3+}$ upon different wavelength excitation.

Figure S12 PL ($\lambda_{ex}$ = 260 nm) spectra of Na$_{0.625}$Ca$_{8.688}$-$x$Al$_{6}$O$_{18}$:$x$Bi$^{3+}$ ($0.003 \leq x \leq 0.04$) sample.
Figure S13 The excitation spectra of Na$_{0.625}$Ca$_{8.668}$Al$_6$O$_{18}$: 0.005Bi$^{3+}$ by monitored different wavelength emission.

Figure S14 The excitation spectra of Na$_{0.625}$Ca$_{8.668}$Al$_6$O$_{18}$: 0.02Bi$^{3+}$ by monitored different
Figure S15 The excitation spectra of Na$_2$Ca$_{7.98}$Al$_6$O$_{18}$:0.02Bi$^{3+}$ by monitored different wavelength emission.

Figure S16 The temperature dependent emission spectra of Na$_{0.625}$Ca$_{8.668}$Al$_6$O$_{18}$:0.02Bi$^{3+}$ ranging from 80 to 300 K;
Figure S17 The normalized time-resolved photoluminescence (TRPL) spectra of $\text{Na}_5\text{Ca}_{7.98}\text{Al}_6\text{O}_{18}:0.02\text{Bi}^{3+}$ at 10 K.

Figure S18 Configurational coordinate diagram of the ground state and four split excited states of $\text{Na}_{0.625}\text{Ca}_{8.668}\text{Al}_6\text{O}_{18}:0.02\text{Bi}^{3+}$
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.

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

Figure S20 Thermal imaging of the WLED driven at different currents
Figure S21 The spectra of 446 nm chip with YAG:Ce\textsuperscript{3+} and 275 nm chip with Na\textsubscript{2}Ca\textsubscript{7.98}Al\textsubscript{6}O\textsubscript{18}:0.02Bi\textsuperscript{3+}.

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

<table>
<thead>
<tr>
<th>Samples</th>
<th>(\lambda_{ex}) (nm)</th>
<th>(\lambda_{em}) (nm)</th>
<th>FWHM (nm)</th>
<th>CCT (K)</th>
<th>CIE</th>
<th>(R_a)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr\textsubscript{5}Ga\textsubscript{4}O\textsubscript{9}:Bi\textsuperscript{3+}</td>
<td>330</td>
<td>530</td>
<td>~200</td>
<td>5896</td>
<td>(0.320,0.466)</td>
<td>79</td>
<td>S1</td>
</tr>
<tr>
<td>Ca\textsubscript{3}Ga\textsubscript{4}O\textsubscript{9}:Bi\textsuperscript{3+}</td>
<td>370</td>
<td>510</td>
<td>~120</td>
<td>8085</td>
<td>(0.250,0.420)</td>
<td>50.5</td>
<td>S2</td>
</tr>
<tr>
<td>Ba\textsubscript{4}Y\textsubscript{3}O\textsubscript{9}:Bi\textsuperscript{3+}</td>
<td>350</td>
<td>610</td>
<td>~150</td>
<td>3720</td>
<td>(0.476,0.445)</td>
<td>95</td>
<td>S3</td>
</tr>
<tr>
<td>Ba\textsubscript{4}Y\textsubscript{3}O\textsubscript{9}:Bi\textsuperscript{3+}</td>
<td>350</td>
<td>580</td>
<td>~180</td>
<td>4808</td>
<td>(0.447,0.479)</td>
<td>94</td>
<td>S3</td>
</tr>
<tr>
<td>Ba\textsubscript{2}ZnGe\textsubscript{2}O\textsubscript{7}:Bi\textsuperscript{3+}</td>
<td>395</td>
<td>500, 620</td>
<td>-</td>
<td>3942</td>
<td>(0.369,0.311)</td>
<td>84.6</td>
<td>S4</td>
</tr>
<tr>
<td>Ba\textsubscript{2}MgGe\textsubscript{2}O\textsubscript{7}:Bi\textsuperscript{3+}</td>
<td>395</td>
<td>500, 620</td>
<td>-</td>
<td>4466</td>
<td>(0.343,0.301)</td>
<td>98.9</td>
<td>S4</td>
</tr>
<tr>
<td>Na\textsubscript{2}Ca\textsubscript{3}Nb\textsubscript{2}O\textsubscript{9}:Bi\textsuperscript{3+}</td>
<td>365</td>
<td>600</td>
<td>~150</td>
<td>3748</td>
<td>(0.410,0.420)</td>
<td>88.6</td>
<td>S5</td>
</tr>
<tr>
<td>CSMKPO:0.02Eu\textsuperscript{2+}</td>
<td>330</td>
<td>490</td>
<td>~175</td>
<td>5186</td>
<td>(0.340,0.346)</td>
<td>89</td>
<td>S6</td>
</tr>
<tr>
<td>YTaO\textsubscript{4}:0.03Bi\textsuperscript{3+}</td>
<td>365</td>
<td>500</td>
<td>~225</td>
<td>9449</td>
<td>(0.274,0.323)</td>
<td>77.8</td>
<td>S7</td>
</tr>
<tr>
<td>GAGO:0.06Ce\textsuperscript{3+}</td>
<td>460</td>
<td>575</td>
<td>~150</td>
<td>3778</td>
<td>(0.390,0.380)</td>
<td>73</td>
<td>S8</td>
</tr>
<tr>
<td>Ba\textsubscript{2}Y(SiO\textsubscript{4})\textsubscript{2}:Eu\textsuperscript{2+}</td>
<td>350</td>
<td>600</td>
<td>~200 nm</td>
<td>3530</td>
<td>(0.402,0.371)</td>
<td>83.5</td>
<td>S9</td>
</tr>
<tr>
<td>Ca\textsubscript{3}+Z5Mg\textsubscript{2}+PO\textsubscript{4}:Eu\textsuperscript{2+}</td>
<td>365</td>
<td>575</td>
<td>-</td>
<td>3788</td>
<td>(0.385,0.365)</td>
<td>85</td>
<td>S10</td>
</tr>
<tr>
<td>NaLi\textsubscript{5}Si\textsubscript{3}O\textsubscript{7}:Eu\textsuperscript{2+}</td>
<td>365</td>
<td>585</td>
<td>-</td>
<td>6599</td>
<td>(0.312,0.322)</td>
<td>82.9</td>
<td>S11</td>
</tr>
<tr>
<td>BaSrMg(PO\textsubscript{4})\textsubscript{2}:Eu\textsuperscript{2+}</td>
<td>385</td>
<td>460, 550</td>
<td>-</td>
<td>5892</td>
<td>(0.320,0.330)</td>
<td>84</td>
<td>S12</td>
</tr>
<tr>
<td>Na\textsubscript{2}Ca\textsubscript{7.98}Al\textsubscript{6}O\textsubscript{18}:0.02Bi\textsuperscript{3+}</td>
<td>280</td>
<td>590</td>
<td>228 nm</td>
<td>5577</td>
<td>(0.331,0.381)</td>
<td>84.2</td>
<td>This work</td>
</tr>
</tbody>
</table>
Figure S22 The synthesis process of the fabricated anti-counterfeiting rose label.

References