Electronic Supplementary Information

A red phosphor BaTiF₆:Mn⁴⁺: reaction mechanism, microstructures, optical properties, and applications for white LEDs

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**Figure S1.** XRD patterns of the as-synthesized red phosphors BaTiF₆:Mn⁴⁺ obtained from etching Ti(OC₄H₉)₄ in HF at (a) 80 °C, (b) 120 °C, and 240 °C for 20 h.
Figure S2. XRD patterns and SEM images of raw materials (a) TiO$_2$ nanoparticles hydrolyzed from Ti(OC$_4$H$_9$)$_4$, (b) TiO$_2$ and (c) BaF$_2$ commercially obtained.
**Figure S3.** XPS survey spectrum of red phosphor BaTiF$_6$:Mn$^{4+}$.

The binding energy of BaTiF$_6$:Mn$^{4+}$ was examined by x-ray photoelectron spectroscopy (XPS, ESCALAB MKII), and all the peaks were calibrated by using C1s at 284.60 eV as the reference.
Figure S4. SEM the as-synthesized red phosphors BaTiF$_6$·Mn$^{4+}$ from Ti(OR)$_4$ at (a) 80, (b) 120, (c) 180, (d) 240 °C for 20 h, and from TiO$_2$ at (e) 80, (f) 120, (g) 180, (h) 240 °C for 20 h,
**Figure S5.** Thermogravimetrics (TG) and different scanning calorimeter (DSC) graphs of as synthesized BaTiF₆:Mn⁴⁺ under N₂ atmosphere. The data were obtained on TG analysis and DSC (Netzsch STA 449C, at a heating rate of 10K/min).

**Figure S6.** Raman spectra of the as-synthesized red phosphor (a) BaTiF₆:Mn⁴⁺ and (b) undoped BaTiF₆ measured on a JY-T64000 Raman spectroscopy at room temperature. Note: both samples are prepared from Ti(OC₄H₉)₄ and the wavelength of the laser excitation is 632.8 nm (1.96 eV, 3 mW).
**Figure S7.** The structure projection of BaTiF$_6$:Mn$^{4+}$ plotted by software Diamond 3.1.

**Figure S8.** Emission spectra (ex=460 nm) of the as-synthesized red phosphor BaTiF$_6$:Mn$^{4+}$ obtained from starting materials BaF$_2$, HF, KMnO$_4$ and Ti(OC$_4$H$_9$)$_4$ at (a) 80 °C, (b) 100 °C, (c) 120 °C, and (d) 240 °C for 20 h.
**Figure S9.** Dependence of emission spectra of BaTiF$_6$:Mn$^{4+}$ on the concentration of KMnO$_4$ at (a) 0.05, (b) 0.75, (c) 1.0, (d) 1.25, (e) 1.5, (f) 2.0, (g) 2.5 (unit: mmol/L).

**Table S1** The performance parameters of the white LEDs fabricated with InGaN chip, yellow phosphor YAG:Ce, and red phosphor BaTiF$_6$:Mn$^{4+}$. The WLED was examined by a LEE300E UV-Vis-near IR Spectrophotocolorimeter (Everfine photo-E-Infor Co., China) instrument.

<table>
<thead>
<tr>
<th>Coordinates of international d'Eclairage</th>
<th>Intensity (mcd)</th>
<th>Efficiency (lm/W)</th>
<th>Color temperature (K)</th>
<th>Color rendering index</th>
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</thead>
<tbody>
<tr>
<td>(0.366,0.331)</td>
<td>2552.8</td>
<td>121</td>
<td>4073.1</td>
<td>93.13</td>
</tr>
</tbody>
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