## **Supporting Information**

## Phase-Transition-Induced Giant Enhancement of Red Emission in Mn<sup>4+</sup> Doped Fluoride Elpasolite Phosphors

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Figure S1. XRD patterns of trigonal K<sub>2</sub>LiAlF<sub>6</sub> matrixes before and after HF solution treatment.



Figure S2. (a) Structure of  $K_2MnF_6$ , bond lengths and angles of (b) [MnF<sub>6</sub>] octahedrons, (c) [AlF<sub>6</sub>] octahedrons in cubic phase, (d) [Al<sub>1</sub>F<sub>6</sub>] and (e) [Al<sub>2</sub>F<sub>6</sub>] octahedrons in trigonal phase.



Figure S3. The calculated energy levels of  $Mn^{4+}$  (vertical bars) and experimental photoluminescence spectra of cubic  $K_2LiAlF_6$ :  $Mn^{4+}$ .



Figure S4. The calculated energy levels of Mn<sup>4+</sup> (vertical bars) and experimental photoluminescence spectra of trigonal K<sub>2</sub>LiAlF<sub>6</sub>: Mn<sup>4+</sup>.



Figure S5. PL spectra of  $K_2LiAlF_6$ : 3 %Mn<sup>4+</sup> (T-C) and (T-T) phosphors.



Figure S6. Mn concentrations of A-E samples.



Figure S7. (a) XRD patterns, (b) PLE spectra and (c) PL spectra of  $K_2LiAlF_6$ : x %Mn<sup>4+</sup> (x = 1, 2, 3, 4 and 5) (the insert is dependence of the integrated emission intensity).



Figure S8. (a) XRD patterns, (b) PLE spectra and (c) PL spectra of K<sub>2</sub>LiAlF<sub>6</sub>: 3
 %Mn<sup>4+</sup> synthesized for different reaction times (the insert is dependence of the integrated emission intensity).



Figure S9. (a) XRD patterns, (b) PL spectra, (c) PL spectra (the insert is dependence of the integrated emission intensity) and (d) decay of K<sub>2</sub>LiAlF<sub>6</sub>: 3 %Mn<sup>4+</sup> synthesized for different reaction temperatures.



Figure S10. The electron energy loss spectroscopy (EELS) of K<sub>2</sub>LiAlF<sub>6</sub>: 3 %Mn<sup>4+</sup>.



Figure S11. The X-ray photoelectron spectroscopy (XPS) of K<sub>2</sub>LiAlF<sub>6</sub>: 3 %Mn<sup>4+</sup>.

Current (mA)	Ra	R9	CCT (K)	Luminescent efficiency (lm/W)	(x, y)
20	86	81	3498	63.3	(0.396,0.367)
50	85	77	3624	59.9	(0.390,0.362)
100	85	76	3731	55.7	(0.384,0.355)
150	85	75	3841	52.1	(0.378,0.349)
200	84	73	3913	49.7	(0.375,0.347)
250	84	74	3917	49.6	(0.374,0.345)

 Table S1. Typical LED photoelectric parameters under different current.