# Electronic Supplementary Information (ESI)

# Novel $Mn^{4+}$-activated layered oxide-fluoride perovskite $KNaMoO_2F_4$ red phosphor for wide gamut warm white light-emitting diodes backlight

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## Characterizations

The phase composition of $KNaMoO_2F_4:Mn^{4+}$ were measured by a powder diffractometer (X' Pert PRO, Cu Kα, λ = 1.5418 Å). The photoluminescence (PL) spectra were recorded by Edinburgh Instruments (FLS 980) equipped with 450 W xenon lamps as the excitation source. The diffuse refection (DR) spectra of the samples were carried out on an UV-Vis-NIR spectrophotometer (Lambda 950, Perkin Elmer), using $BaSO_4$ as a standard reference. The morphologies of the samples were characterized using a scanning electron microscope (SEM, JSM-6700F). The electron paramagnetic resonance (EPR) spectrum of $K_3TaOF_6:Mn^{4+}$ was obtained on a JES-FA 200 EPR spectrometer. High-resolution transmission electron microscopy (HRTEM) was recorded using a FEI Tecnai G2S-Twin. To investigate the electronic structures of pure $KNaMoO_2F_4$, calculations were performed by the plane-wave pseudopotential method[1] implemented in the CASTEP program based on density functional theory (DFT).[2] The kinetic energy cutoffs of 380 eV and Monkhorst-Pack *k*-point meshes with a density of (4 × 4 × 1) points in the Brillouin zone were chosen.[3]

## References

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2. D. Vanderbilt, *Phys. Rev. B.,* 1990, **41**, 7892-7895.

3. H. J. Monkhorst, J. D. Pack, *Phys. Rev. B.,* 1976, **13**, 5188-5192.

## 1. Tables and Figures

**Table S1.** Rietveld refinement of X-ray diffraction data of $KNaMoO_2F_4$:0.01$Mn^{4+}$.

**Table S2.** Some bond lengths of $KNaMoO_2F_4$.

**Table S3 S4**. Current- and temperature-dependent CCT, Ra and CIE chromaticity coordinates of as-fabricated proof-of-concept w-LED.

**Fig. S1.** XRD patterns of $KNaMoO_2F_4$:x$Mn^{4+}$.

**Fig. S2.** Rietveld refinements of the observed XRD patterns for the $KNaMoO_2F_4$:0.01$Mn^{4+}$.

**Fig. S3.** (a) Calculated energy band structure of $KNaMoO_2F_4$ (b) The DR spectra of $KNaMoO_2F_4$:x$Mn^{4+}$, the inset show the optical energy band based on the DR spectrum.

**Fig. S4.** (a) Room-temperature PL under 475 nm excitation (b) CIE chromaticity coordinate of the $KNaMoO_2F_4$:0.01$Mn^{4+}$ phosphor (c) (d) Integrated emission intensity and fluorescence decay curve of the $KNaMoO_2F_4$:x$Mn^{4+}$ phosphor.

**Fig. S5.** (a) Tanabe-Sugano energy diagram for $Mn^{4+}$. ($3d^3$) in an octahedral crystal field. (b) The relationship between the $Mn^{4+}$:$^2$E energy level and the calculated nephelauxetic ratio in different β hosts.

**Fig. S6.** The PL spectrum of $KNaMoO_2F_4$:0.01$Mn^{4+}$ at 4 K.

**Table S1** Rietveld refinement of X-ray diffraction data of $KNaMoO_2F_4$:0.01$Mn^{4+}$

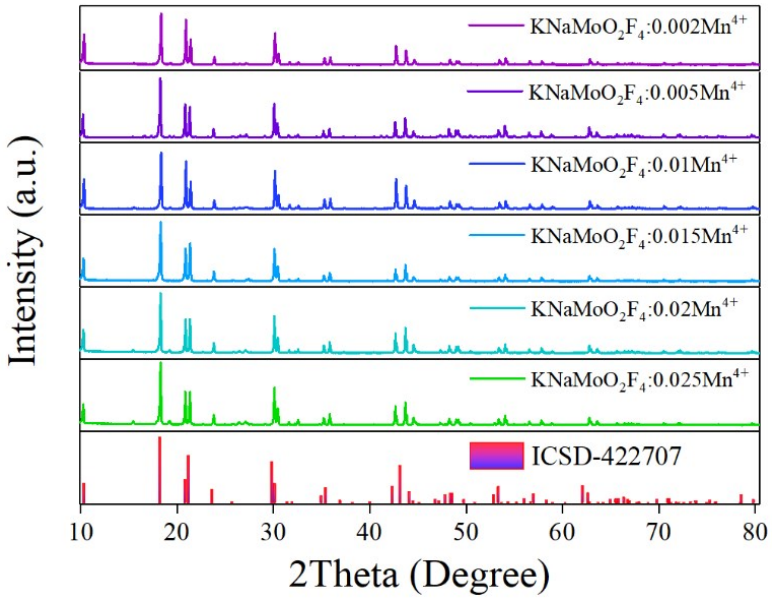
| Formula | $KNaMoO_2F_4$:0.01$Mn^{4+}$ |
|---|---|
| Crystal system | tetragonal |
| Space group | P4/nmm |
| Lattice parametes | |
| a=b (Å) | 5.875 |
| c (Å) | 8.498 |
| α=β=γ (°) | 90 |
| Cell volume (Å$^3$) | 293.376 |
| R-factors | |
| $R_{wp}$(%) | 11.69 |
| $R_p$(%) | 8.45 |

**Table S2** Some bond lengths of $KNaMoO_2F_4$.

| Atom | x | y | z | Bond | Length(Å) | Bond | Length(Å) | Bond | Length(Å) |
|---|---|---|---|---|---|---|---|---|---|
| Na | -0.25 | 0.75 | 0.76 | Na-$O_1$ | 2.3408 | Na-$O_2$ | 2.3360 | Na-F | 2.2766 |
| K | 0.25 | 0.75 | 0.50 | K-$O_2$ | 2.9327 | | | | |
| Mo | 0.25 | 0.25 | 0.76 | Mo-$O_1$ | 1.6718 | Mo-$O_2$ | 2.1110 | Mo-F | 1.9704 |

**Table S3 S4**. Current- and temperature-dependent CCT, Ra and CIE chromaticity coordinates of as-fabricated proof-of-concept w-LED.

| mA | (lm/W) | x | y | CCT | Ra |
|---|---|---|---|---|---|
| 19.95 | 84.32 | 0.3394 | 0.3387 | 4490 | 83.5 |
| 49.96 | 81.43 | 0.3374 | 0.335 | 4476 | 83.3 |
| 99.97 | 75.98 | 0.335 | 0.3306 | 4467 | 83 |
| 149.9 | 71.19 | 0.333 | 0.327 | 4454 | 82.9 |
| 200 | 67.25 | 0.3314 | 0.3243 | 4459 | 82.7 |
| 250 | 63.67 | 0.33 | 0.3219 | 4452 | 82.5 |
| 300 | 60.17 | 0.3284 | 0.3193 | 4452 | 82.4 |
| 349.9 | 57.16 | 0.3276 | 0.3179 | 4445 | 82.2 |
| 399.8 | 53.96 | 0.3261 | 0.3155 | 4445 | 82.2 |
| 449.9 | 51.1 | 0.3253 | 0.3141 | 4442 | 82 |
| Temperature (℃) | (lm/W) | x | y | CCT | Ra |
| 30 | 79.66 | 0.3349 | 0.3346 | 4493 | 83.3 |
| 40 | 78.54 | 0.332 | 0.3318 | 4490 | 83.4 |
| 50 | 77.25 | 0.3275 | 0.3269 | 4497 | 83.6 |
| 60 | 76.32 | 0.323 | 0.3213 | 4500 | 82.2 |
| 70 | 75.47 | 0.3194 | 0.3166 | 4507 | 81.9 |
| 80 | 74.08 | 0.314 | 0.3093 | 4511 | 81 |
| 90 | 72.87 | 0.3102 | 0.3042 | 4517 | 81 |
| 100 | 71.11 | 0.306 | 0.2981 | 4520 | 81.2 |

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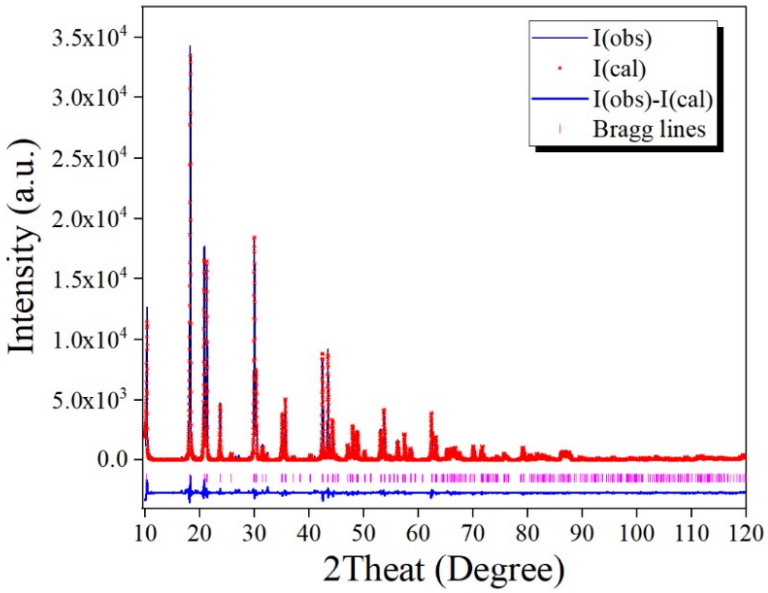


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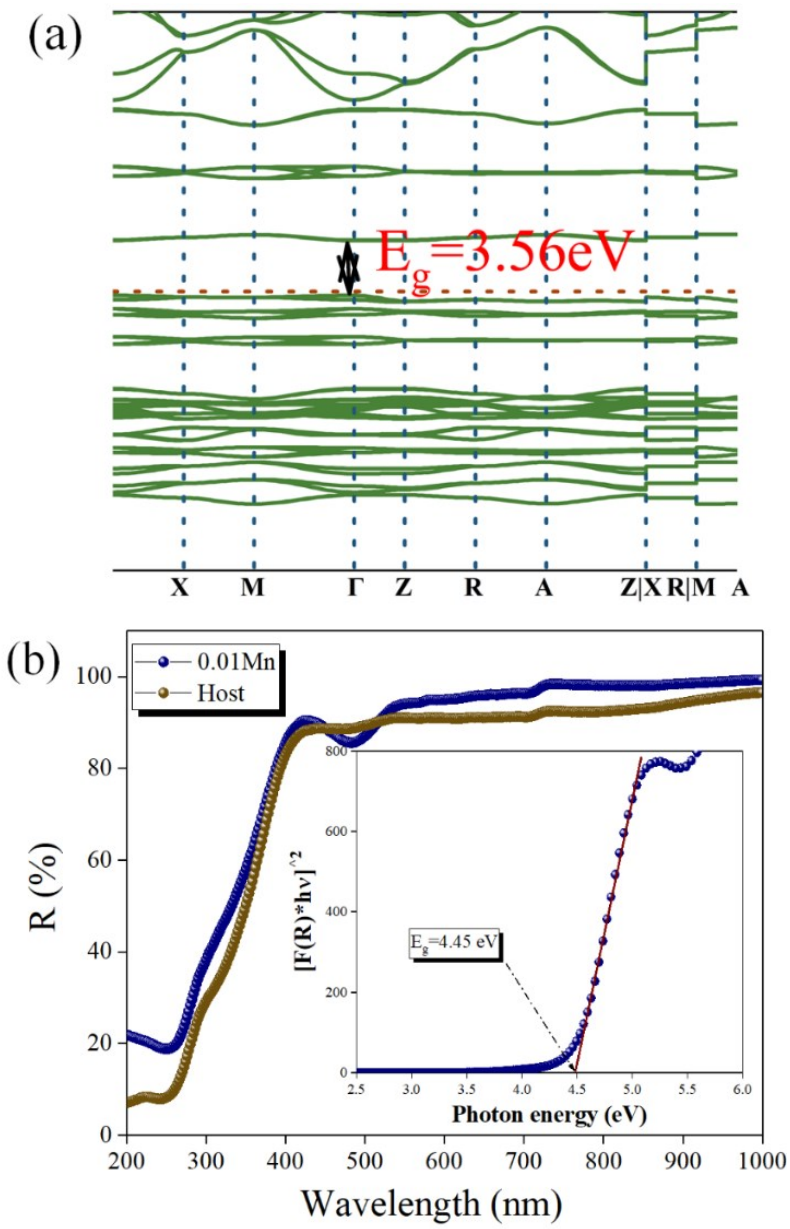


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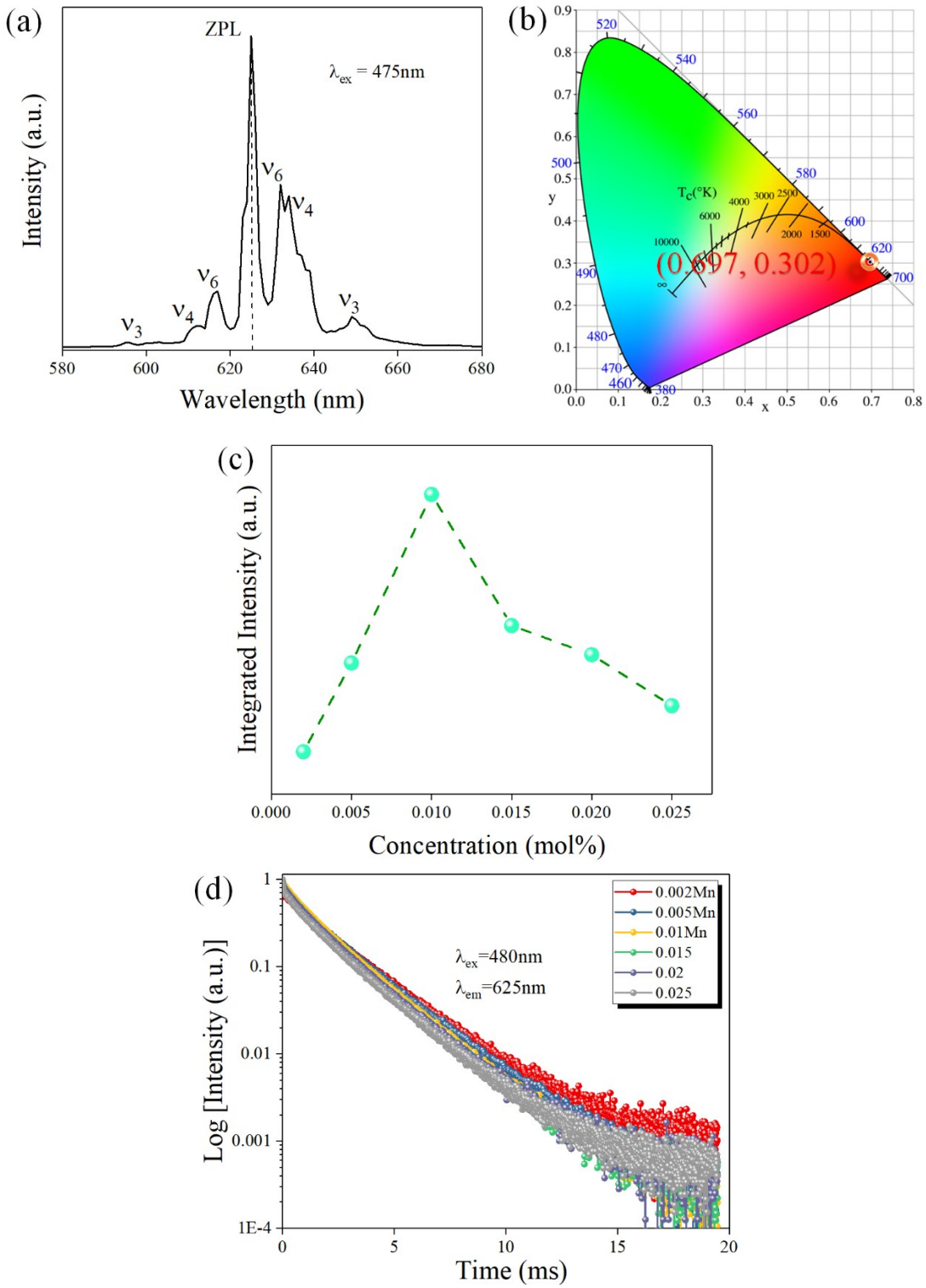


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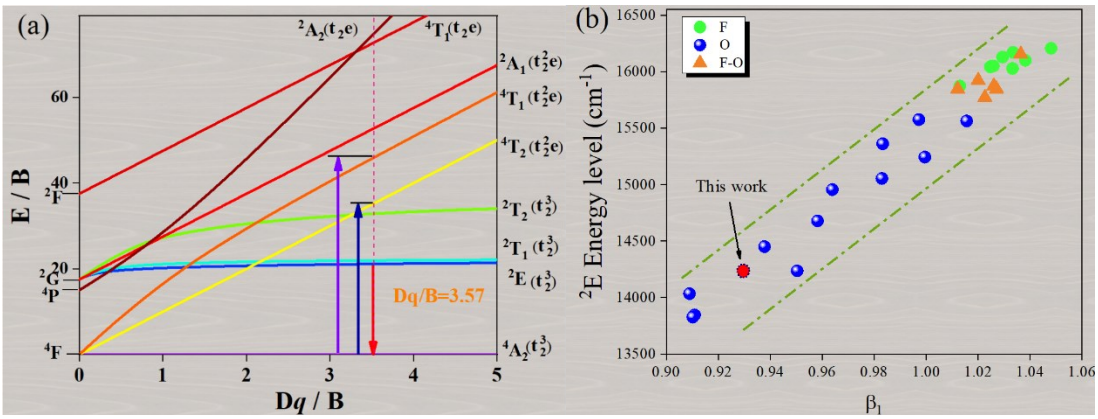


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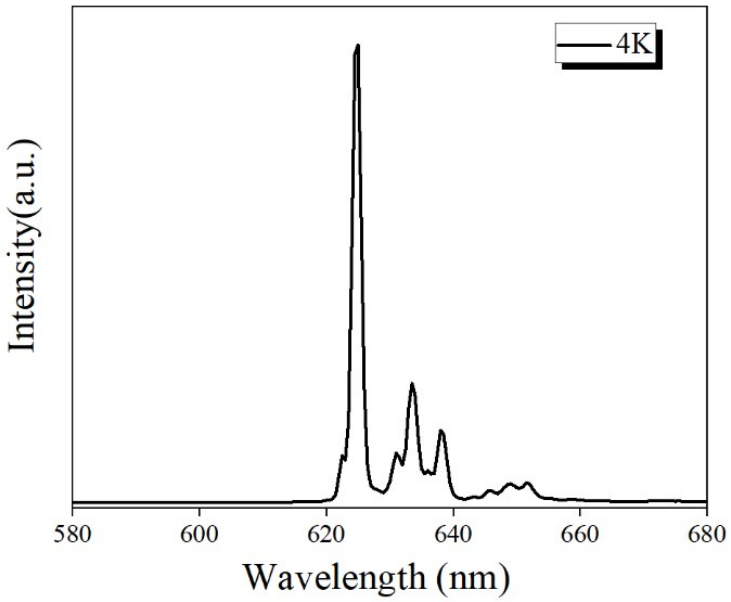


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