

Supporting Information

Harnessing Solid-State Ion Exchange for the Environmentally Benign Synthesis of High-Efficiency Mn⁴⁺-Doped Phosphors

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Experimental Section

Chemicals and materials: K_2TiF_6 , K_2SiF_6 , Na_2TiF_6 , KHF_2 were all purchased from Sigma-Aldrich (China). The K_2MnF_6 crystals were prepared via a reported method.^[1] All chemicals were used as received without further purification.

Synthesis of $\text{K}_2\text{TiF}_6:\text{Mn}^{4+}$ Red Phosphor: The $\text{K}_2\text{TiF}_6:\text{Mn}^{4+}$ red phosphor were synthesized via a mechanochemical synthesis method. In a typical experiment, K_2TiF_6 powder and K_2MnF_6 powder were mixed with together in an agate mortar, then, the mixed powder was thoroughly ground for 30 minutes to obtaine the Mn^{4+} doped K_2TiF_6 phosphor.

Characterization: Powder X-ray diffraction (XRD) patterns of the samples were collected with an X-ray diffractometer (MiniFlex 600, Rigaku) with Cu $\text{K}\alpha_1$ radiation ($\lambda = 0.154187$ nm). The morphologies of the samples were recorded using a scanning electron microscopy SEM (SU1510, Hitachi) equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer. The PL excitation and emission spectra were measured with an Edinburgh Instrument FLS 1000 spectrometer equipped with a 450 W xenon lamp as the excitation sources. The absolute PL quantum yields (QYs) of the phosphor were measured by employing a standard barium sulfate coated integrating sphere (150 mm in diameter, Edinburgh) as the sample chamber that was mounted on the FLS 1000 spectrometer with the entry and output port of the sphere located in 90° geometry from each other in the plane of the spectrometer. A standard tungsten lamp was used to correct the optical response of the instrument.

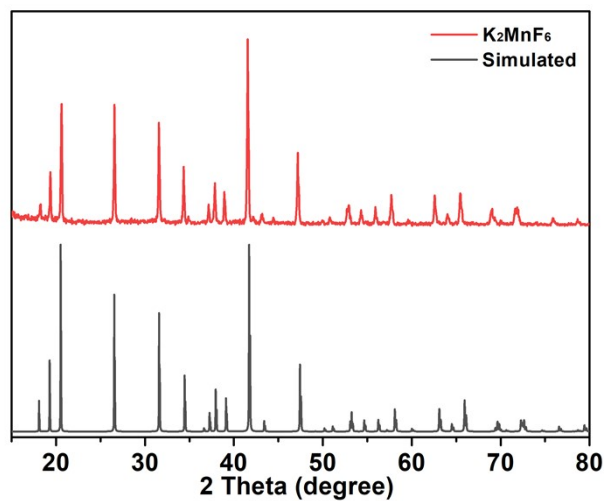


Figure S1. XRD patterns of the K_2MnF_6 crystals.

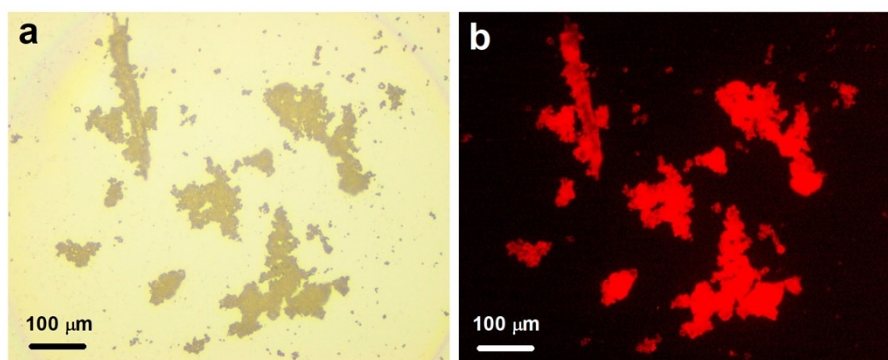


Figure S2. Micrographs of $K_2TiF_6: Mn^{4+}$ phosphor. a) bright field photo; b) fluorescent photo.

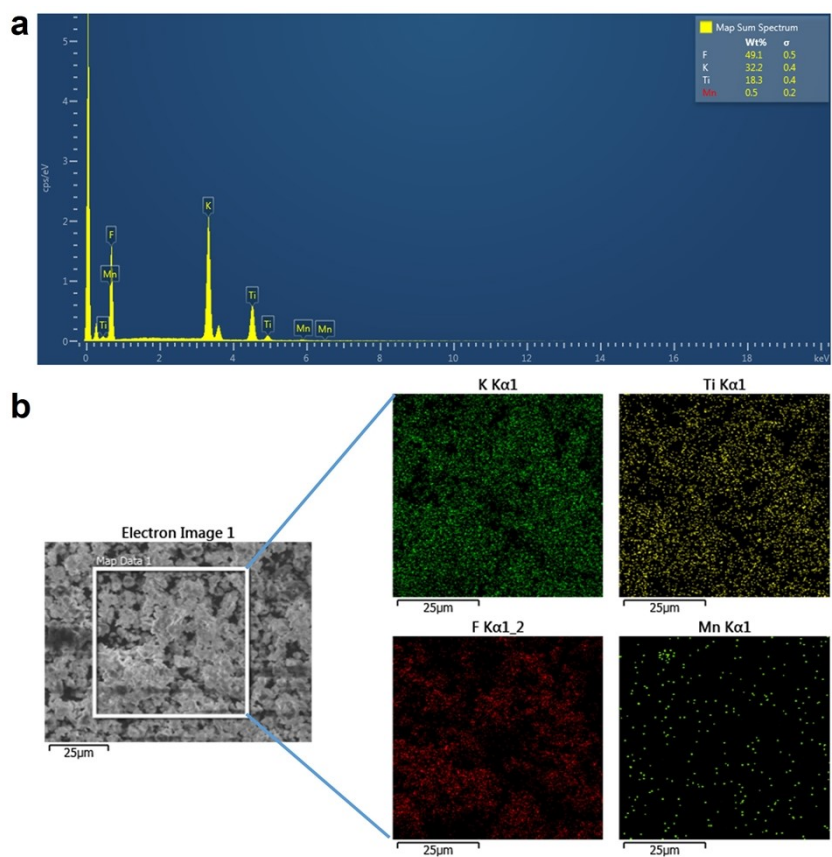


Figure S3. a) The EDS spectrum of the $\text{K}_2\text{TiF}_6:2.5\%\text{Mn}^{4+}$ phosphor. b) The SEM and element mapping images of K, Ti, F and Mn for the $\text{K}_2\text{TiF}_6:2.5\%\text{Mn}^{4+}$ phosphor.

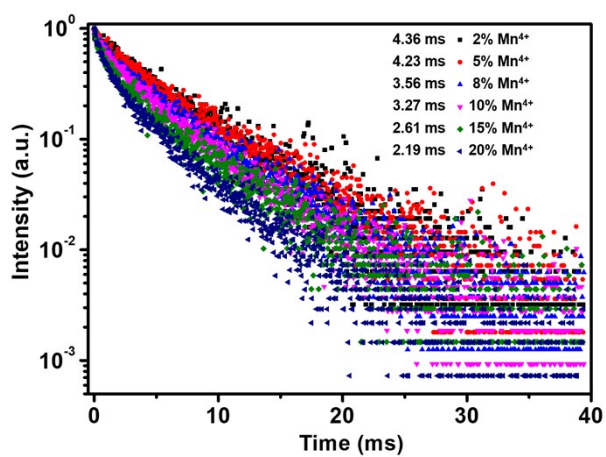


Figure S4. PL lifetimes of the $\text{K}_2\text{TiF}_6:\text{Mn}^{4+}$ sample with different Mn^{4+} doping concentrations.

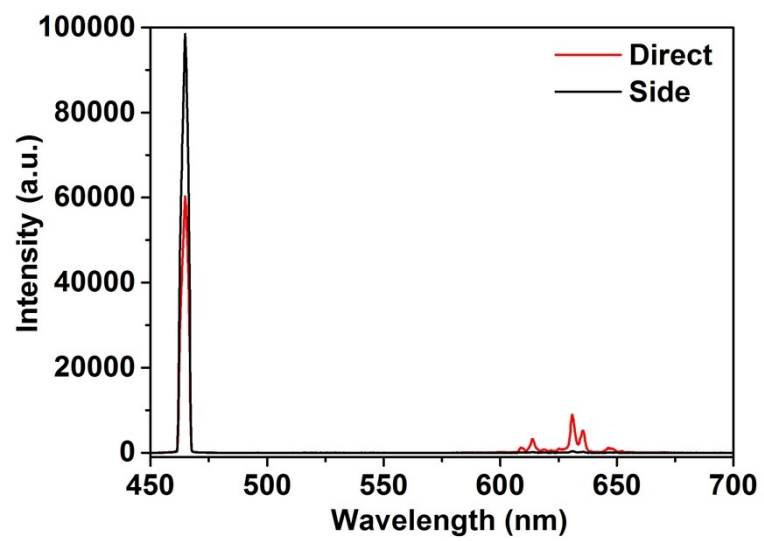


Figure S5. The quantum yield (QY) test spectra of $K_2TiF_6: 10\%Mn^{4+}$ phosphor.

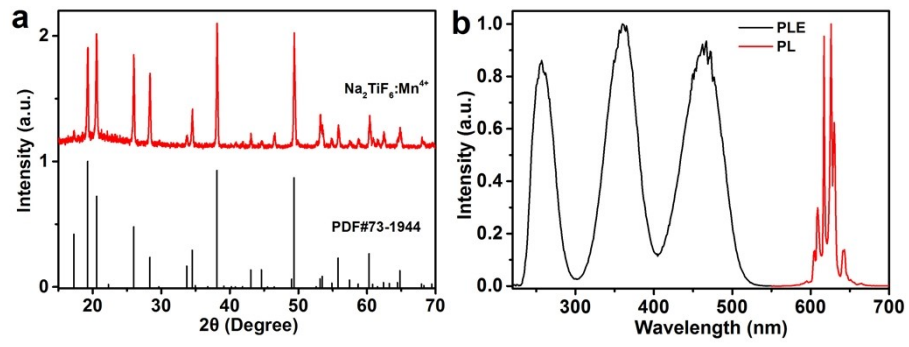


Figure S6. a) XRD patterns of the obtained Na₂TiF₆:Mn⁴⁺ phosphor. b) PL excitation and emission spectra of the obtained Na₂TiF₆:Mn⁴⁺ phosphor.

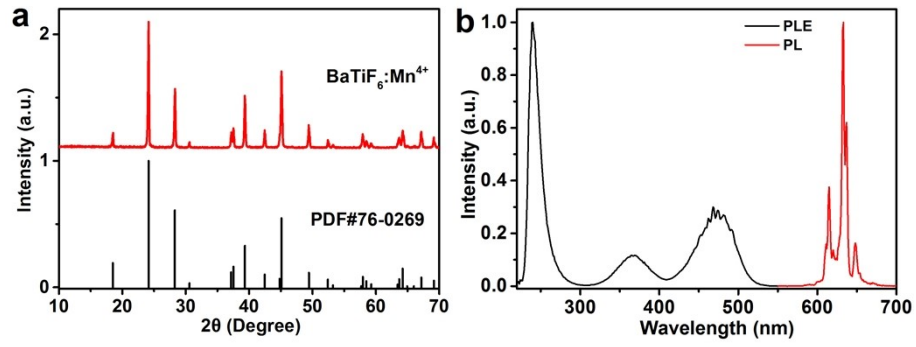


Figure S7. a) XRD patterns of the obtained BaTiF₆:Mn⁴⁺ phosphor. b) PL excitation and emission spectra of the obtained BaTiF₆:Mn⁴⁺ phosphor.

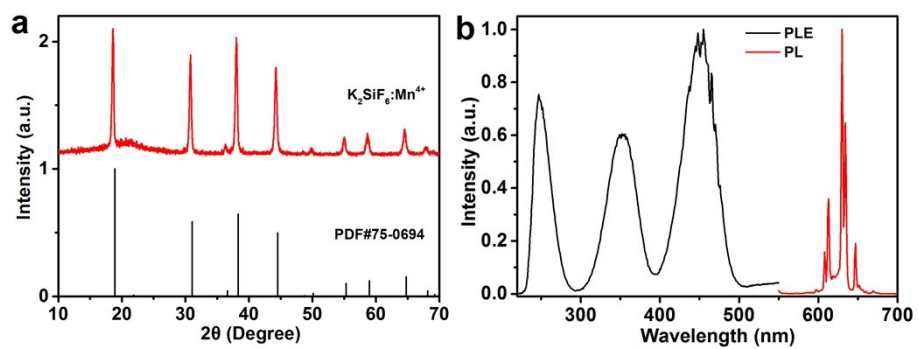


Figure S8. a) XRD patterns of the obtained $K_2SiF_6:Mn^{4+}$ phosphor. b) PL excitation and emission spectra of the obtained $K_2SiF_6:Mn^{4+}$ phosphor.

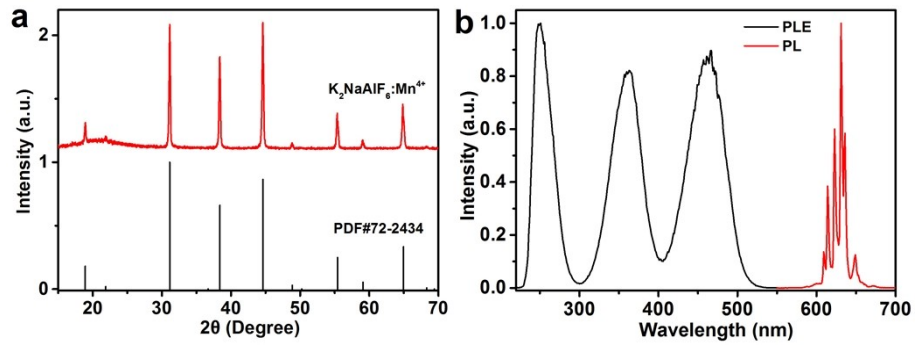


Figure S9. a) XRD patterns of the obtained $K_2NaAlF_6:Mn^{4+}$ phosphor. b) PL excitation and emission spectra of the obtained $K_2NaAlF_6:Mn^{4+}$ phosphor.

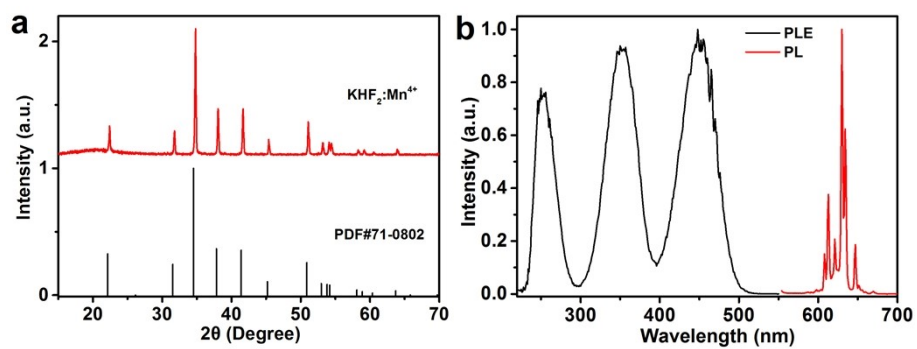


Figure S10. a) XRD patterns of the obtained KHF_2 phosphor. b) PL excitation and emission spectra of the obtained KHF_2 phosphor.

References

- [1] Y. Liu, G. Gao, L. Huang, Y. Zhu, X. Zhang, J. Yu, B. S. Richards, T. Xuan, Z. Wang and J. Wang, *J. Mater. Chem. C*, 2018, **6**, 127-133.