

## Electronic Supplementary Information

### Design, preparation, and optimized luminescence of a dodec-fluoride phosphor $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}:\text{Mn}^{4+}$ for warm WLEDs application

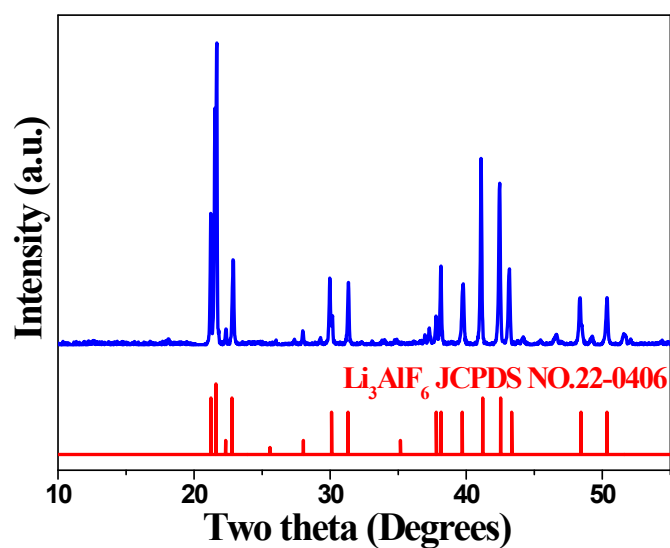
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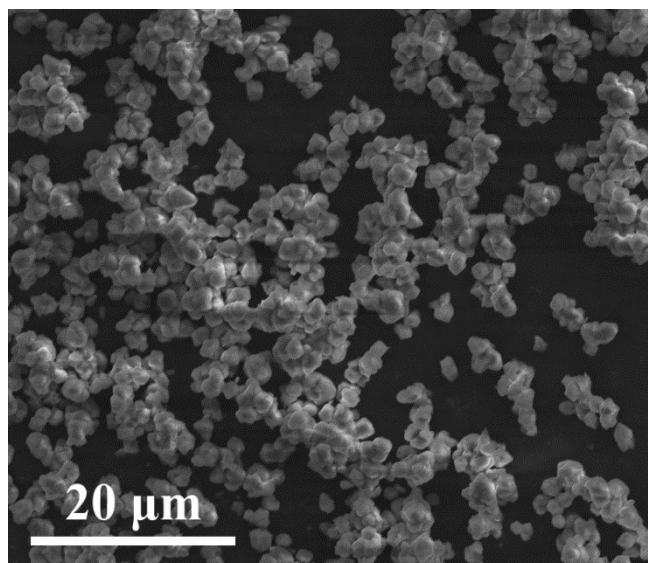
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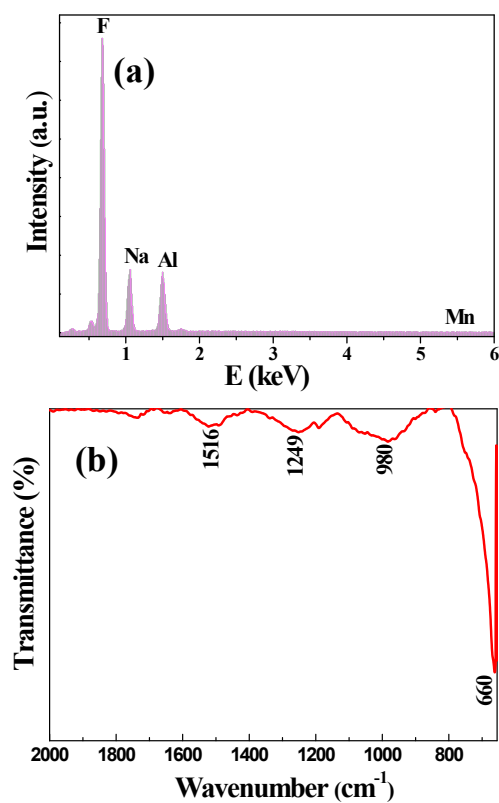
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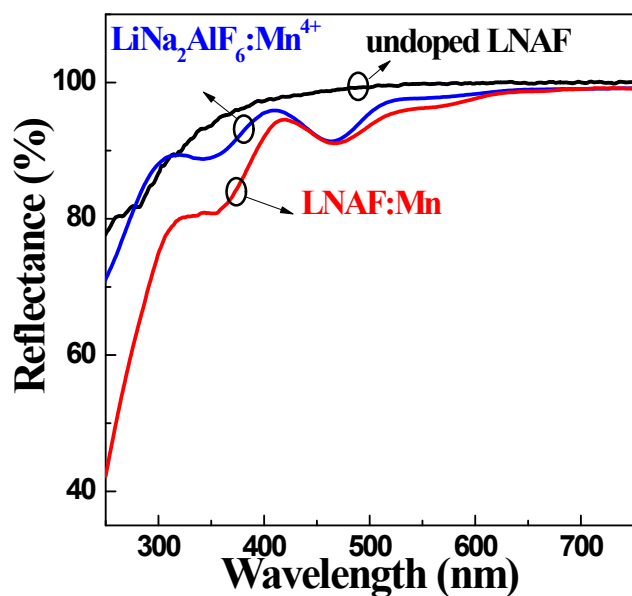
**Figure S1.** X-ray diffraction pattern of the sample obtained in the reaction with molecular ratio of  $\text{LiF}/\text{AlF}_3$  at 3:1 absent of  $\text{NaF}$  as compared with the standard data of  $\text{Li}_3\text{AlF}_6$  in JCPDS no. 22-0406.



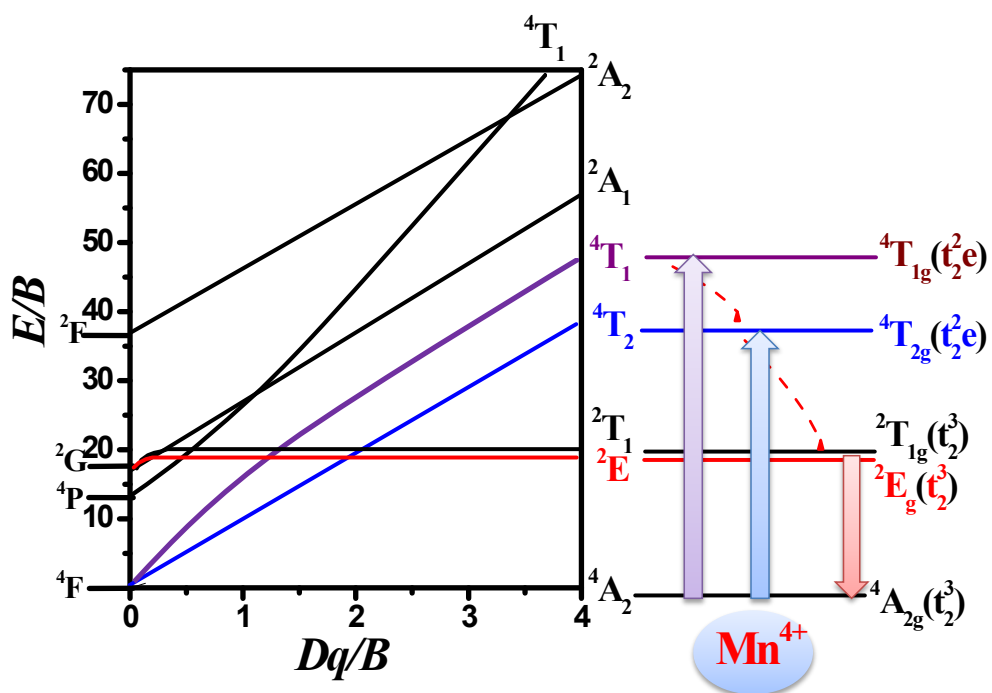
**Figure S2.** SEM images of  $\text{LiNa}_2\text{AlF}_6:\text{Mn}^{4+}$  phosphor obtained at room temperature.



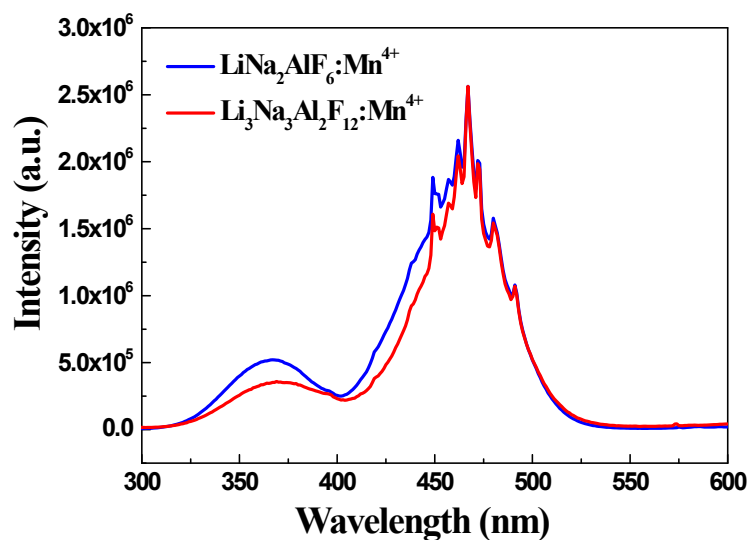
**Figure S3.** (a) EDS and (d) IR spectrum of red phosphor  $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}:\text{Mn}^{4+}$ .



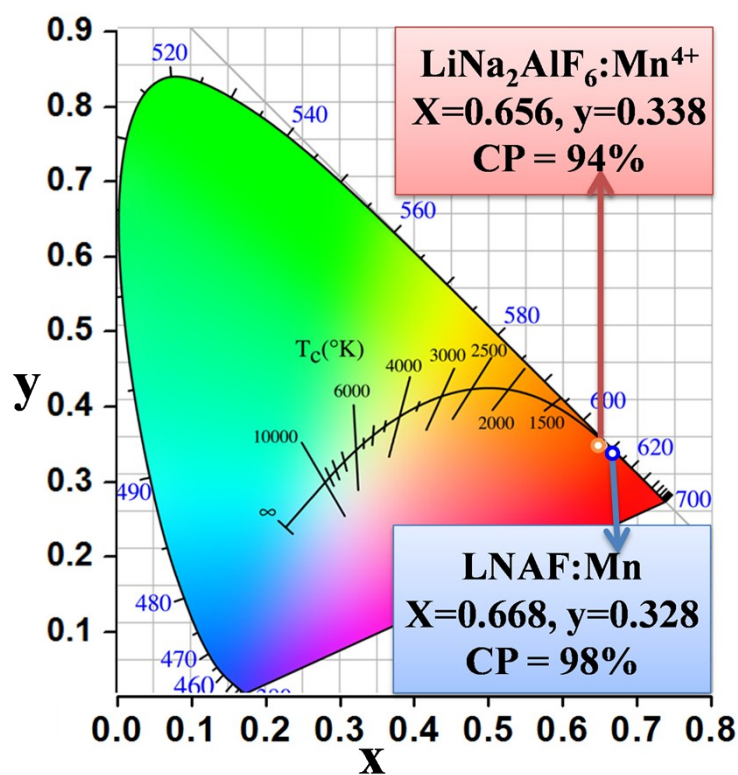
**Figure S4.** The powder diffuse reflectance spectra of undoped  $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$  and two red phosphors  $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}:\text{Mn}^{4+}$  and  $\text{LiNa}_2\text{AlF}_6:\text{Mn}^{4+}$ .



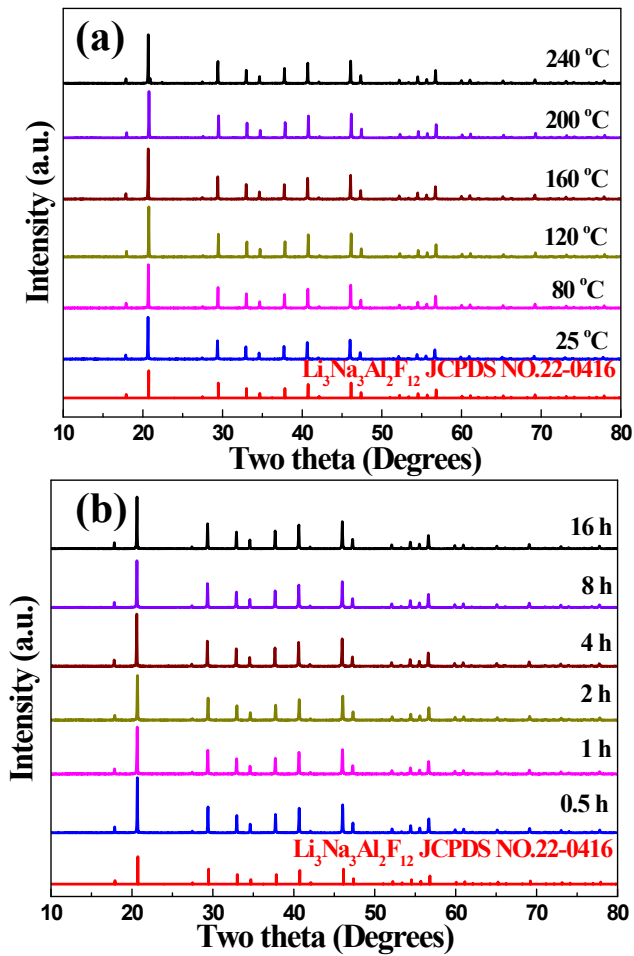
**Figure S5.** Tanabe-Sugano energy level diagram for  $5d^3$  electron configuration of  $\text{Mn}^{4+}$  in the center of octahedron.



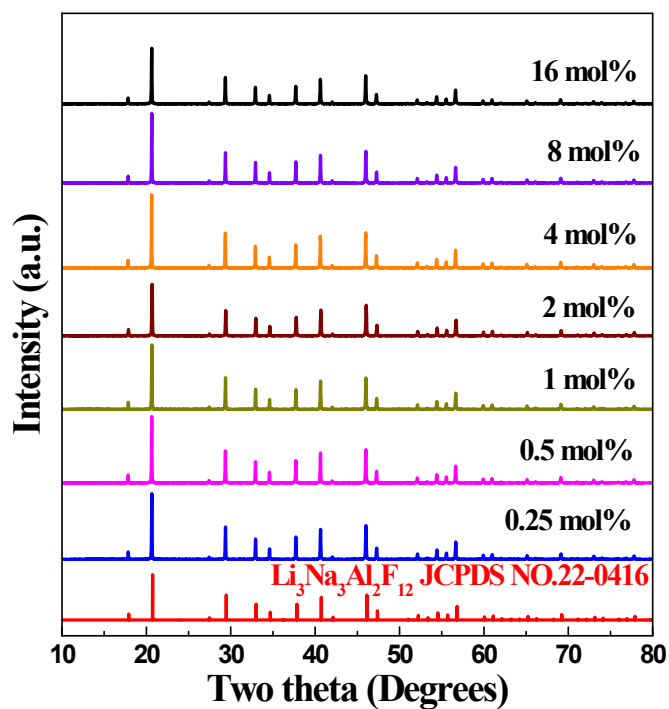
**Figure S6.** The excitation spectra of LNAF:Mn and  $\text{LiNa}_2\text{AlF}_6:\text{Mn}^{4+}$  with modified intensity.



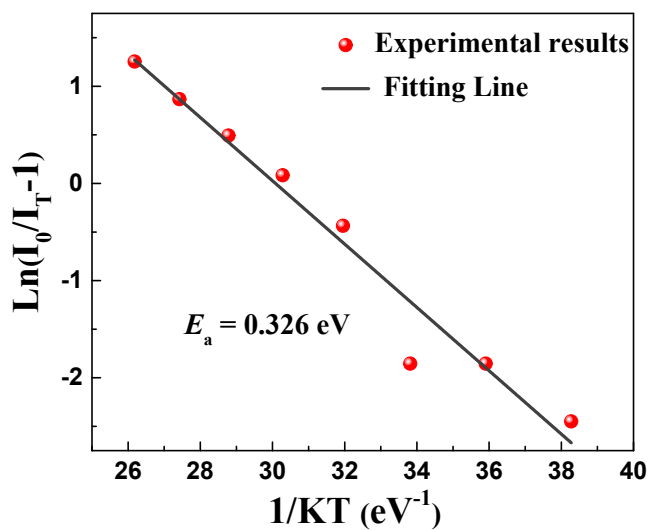
**Figure S7.** CIE chromaticity coordinates and color purity of the as-obtained red phosphors  $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}:\text{Mn}^{4+}$  and  $\text{LiNa}_2\text{AlF}_6:\text{Mn}^{4+}$ .



**Figure S8.** X-ray diffraction patterns of the red phosphor  $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}:\text{Mn}^{4+}$  obtained (a) at various temperatures and (b) for different reaction times compared with the standard data of  $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$  in JCPDS no. 22-0416.



**Figure S9.** Dependence of x-ray diffraction patterns of the red phosphor  $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}:\text{Mn}^{4+}$  on ratio of  $\text{K}_2\text{MnF}_6/\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$ .



**Figure S10.** Arrhenius fitting of the emission intensity of the phosphor  $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}:\text{Mn}^{4+}$  decreased with temperature increasing.

**Table S1.** Details of Rietveld Refinement of  $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}:\text{Mn}^{4+}$  and  $\text{LiNa}_2\text{AlF}_6:\text{Mn}^{4+}$ .

<b>Formula</b>	<b><math>\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}</math></b>	<b><math>\text{LiNa}_2\text{AlF}_6</math></b>
CSD number	9923	96477
Formula weight	371.73	193.89
Crystal system	Cubic	monoclinic
Space group	Ia-3d	P121/n1
D (calc)	2.77	3.02
a (Å)	12.122(2)	5.2842(1)
b (Å)	12.122(2)	5.3698(1)
c (Å)	12.122(2)	7.5063(2)
V (Å <sup>3</sup> )	1781.24	212.99
Z	8	2
Space group number	230	14
a	90°	90°
β	90°	89.98(1)°
γ	90°	90°