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Supporting information of

Set of manganese ions activated fluoride phosphors (A_2BF_6:Mn^{4+}, A=K, Na, B=Si, Ge, Ti): Synthesis below 0 °C and efficient room-temperature photoluminescence

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Table s1 Specific information of the raw materials used in our synthesis experiment.

Raw materials	Source	Grade	Function
HF	Aladdin Chemistry Co., China	49wt.% in H2O, 99.99998% metal basis	Solvent, Reactant
KHF_2	Aikeshiji Chemistry Co., China	AR, 99%	Reactant, Catalyzer
$NaHF_2$	Aikeshiji Chemistry Co., China	98%	Reactant, Catalyzer
$KMnO_4$	Guanchen Co. China	99.3%	Reactant, Oxidizer
H_2O_2	Aladdin Chemistry Co., China	AR, 30wt.% in H2O	Reactant, deoxidizer
K_2TiF_6	Aladdin Chemistry Co., China	AR, 99.5%	Reactant, Ti source
H_2SiF_6	Aladdin Chemistry Co., China	GR, 30-32wt.%	Reactant, Si source
GeO_2	Aladdin Chemistry Co., China	99.99% metal basis, >200 mesh	Reactant, Ge source

Table s2 Energetic positions of the ZPL lines and the major phonon sidebands in the PL spectra of the synthesized phosphors.

Fluorides	ZPL(eV)	Phonon sideband1		Phonon sideband2		Phonon sideband3	
		S.	Anti-S.	S.	Anti-S.	S.	Anti-S.
K_2TiF_6:Mn^{4+}	1.9916	1.9637	2.0182	1.9489	2.0333	1.9133	2.0643
K_2GeF_6:Mn^{4+}	1.9945	1.9657	2.0205	1.9521	2.0365	1.9138	2.0701
K_2SiF_6:Mn^{4+}	1.9954	1.9664	2.0226	1.9531	2.0375	1.9154	2.0746
Na_2SiF_6:Mn^{4+}	2.0072	1.9772	2.0362	1.9648	2.0505	1.9285	2.0859

Noted that "S." denotes the peak positions of the Stokes phonon sidebands, while "Anti-S." represents the peak positions of the anti-Stokes bands.

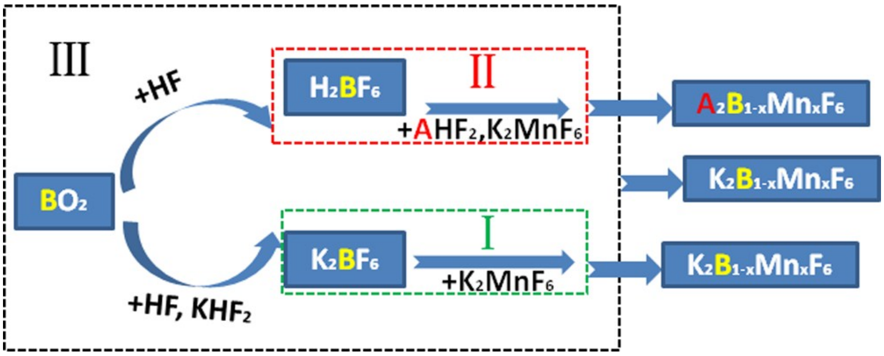

Figure s1. A schematic diagram showing the three synthesizing schemes in the preparation of red phosphors: I for synthesizing KTFM; II for both KSFM and NaSFM; III for KGFM.

Figure s1 depicts the three synthesizing schemes for the fluoride phosphors based on the B compounds. In scheme I, K_2BF_6 compound is directly adopted to react with K_2MnF_6 via the cation exchange between B^{4+} and Mn^{4+}. In scheme II, H_2BF_6 solution is used to react with the admixture of K_2MnF_6 and AHF_2. Being different from the cation exchange reaction, this kind of reaction directly produces the final product via no generation of K_2BF_6 compound. In synthesizing scheme III, the oxide of BO_2 is employed as B source materials, which could be the most complex one since the two above-described reaction mechanisms may simultaneously occur in it, leading to the generation of two different hexagonal phases during this process.

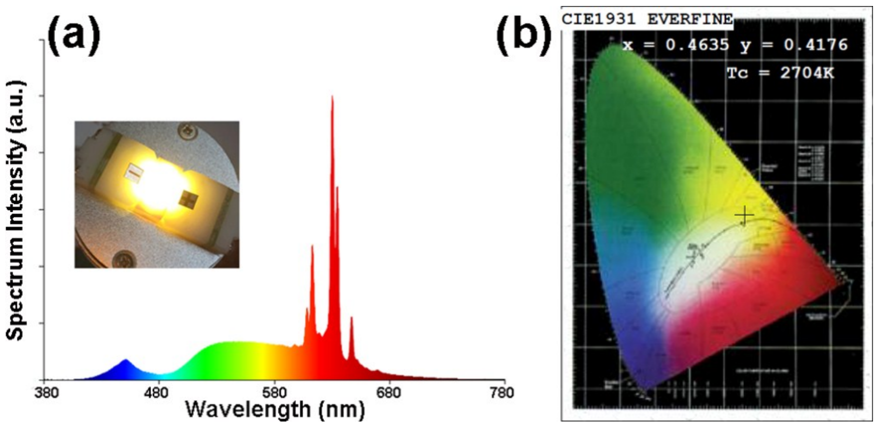

Figure s2. (a) Luminescence spectrum of a warm white LED prepared with the admixture of the KSFM red phosphor and the commercial YAG:Ce^{3+} yellow phosphor plus a 450 nm InGaN/GaN blue LED. The inset is a photo of the warm white LED; (b) The chromaticity coordinates of the LED with CCT of 2704 K at the position of (0.4635, 0.4176).

Figure s2(a) illustrates the full color luminescence spectrum of a warm white LED device at room temperature, which is prepared with a 450 nm InGaN/GaN blue LED + a coating layer of the mixed phosphor of red KSFM and yellow YAG:Ce^{3+}. The inset figure is a photon of the warm white LED with a color coordination of (0.4635, 0.4176) shown in **Figure s2(b)**. The warm white light of the composite LED possesses a low correlated color temperature (CCT) of 2704 K and a high color render index (CRI) of 81.2. And its luminous efficiency is as high as 122 lm/W. These good properties indicate a promising application of our phosphors in the back-light displaying and indoor lighting fields.