Supplementary materials

Organic-inorganic hybrid K_2TiF_6:Mn^{4+} red emitting phosphor with remarkable improvement of emission and thermal stability luminescent thermal stability

Yan Yu [a], *Lin Wang* [a], *Daishu Deng* [a], *Xue Zhong* [a], *Jiawei Qiang* [a], *Tianman Wang* [a], *Chunxiang Wu* [a], *Sen Liao* [*ab], *Yingheng Huang* [*a,b]

[a] *School of Chemistry and Chemical Engineering, Guangxi University, Nanning, Guangxi, 530004, China*

[b] *Guangxi Key Laboratory of Processing for Non-ferrous Metals and Featured Materials, School of Resources, Environment and Materials, Guangxi University, Nanning, Guangxi, 530004, China*

1 Experimental and methodology

1.1 Reagent and apparatus

Most chemicals were reagent-grade pure products purchased from the Sinopharm Chemical Reagent Co. Ltd., China. The crystal information of the powder samples was obtained by X-ray diffractometer (XRD) equipped with a graphite monochromator using Rigaku D/max 2500 V and monochromatic CuKα radiation (λ=0.154178 nm). A Hitachi S-3400 Scanning Electron Microscope (SEM) was used to obtain an image of the sample, and an additional energy dispersive X-ray spectrometer (EDS) was used to determine the elemental composition of the sample. A Horiba Fluoro Max-4-R F6000 spectrophotometer equipped with a xenon lamp as the excitation source was used to record the photoluminescence excitation and emission spectra (PLE/PL) at room temperature. The luminescent decay curve and the photo luminescent quantum yield were obtained with an Edinburgh FLS980 fluorescence spectrophotometer. The thermal analysis was performed in a NETZSCH STA 409 PC/PG thermogravimetric analyzer with a heating rate of 10 °C/min and pure nitrogen (99.999%) as a protective atmosphere with a flow rate of 20 ml/min. The performance of WLEDs was obtained using an auto-temperature LED opto-electronic analyser (LATA-1000, Everfine).

1.2 Preparation of samples

1.2.1 K_2MnF_6

Firstly, 4.5 g $KMnO_4$ and 45 g KHF_2 (99.5%) were dissolved in 150 mL HF (40%) solution. After stirring for 30 min, 3.2 mL (30%) H_2O_2 was slowly added to the mixture. Subsequently, the deep purple solution gradually turned brown and a yellow precipitate is produced. Finally, it was washed several times with acetone and dried at 70 °C for 2 h to obtain K_2MnF_6 powder.

1.2.2 Commercial-K_2TiF_6:0.06Mn^{4+} (CKTF:Mn^{4+})

Firstly, weigh 15 ml HF (40%) and 2.5 g $KF{\bullet}2H_2O$ into a plastic beaker and stir with a magnetic stirrer until the $KF{\bullet}2H_2O$ is completely dissolved. Then 1.5 mmol (0.37 g) K_2MnF_6 was added to the beaker and stirred for 30 min. 23.5 mmol (5.64 g) the purchased K_2TiF_6 powder was added to the beaker and stirred for 30 min. Finally, the mixture was left for 24 h, washed with acetone several times, and dried at 70 °C for 3 h to obtain sample (0) CKTF:Mn^{4+}.

1.2.3 K_2TiF_6 (KTF)

Firstly, 225 mmol (31.10 g) K_2CO_3, and 32 ml H_2O were added to the plastic beaker and stirred for 30 min to obtain the mixed solution. Then, 225 mmol (73.74 g) H_2TiF_6 (50%) was slowly added to the plastic beaker and stirred to obtain the mixture. The mixture was ground with an agate mortar for 1 h. Finally, the mixture was dried at 120 °C for 3 h to obtain KTF.

1.2.4 K_2TiF_6:0.06Mn^{4+} (KTF:Mn^{4+})

Firstly, 15 ml HF (40%) and 2.5 g KF•2H_2O were weighed and added to a plastic beaker and stirred with a magnetic stirrer until KF•2H_2O was completely dissolved. Then 1.5 mmol (0.37 g) K_2MnF_6 was added to the beaker and stirred for 30 min. 23.5 mmol (5.64 g) KTF powder was added to the beaker and stirred for 30 min. Finally, the mixture was allowed to stand for 24 h, washed several times with acetone and dried at 70 °C for 3 h to obtain sample (i) KTF:Mn^{4+}.

1.2.5 K_2TiF_6:*y*$HO(CH_2)_2NH_3^+$ (KTF:*y*$MEAH^+$)

Firstly, 225 mmol (73.74 g) H_2TiF_6 (50%) and 45 mmol (2.74 g) $HO(CH_2)_2NH_2$ (MEA) (y = molar ratio of MEA / Ti) were added to a plastic beaker on the one hand and stirred for 30 min to obtain a mixed solution (I). On the other hand to a plastic beaker 202.5 mmol (27.99 g) K_2CO_3 and 32 ml H_2O were added to another plastic beaker and stirred for 30 min to obtain the mixed solution (II). Then the mixed solution (II) was slowly added to the mixed solution (I) and stirred to obtain the mixture. The mixture was ground with agate mortar for 1 h. Finally, the mixture was dried at 120 °C for 3 h to obtain KTF:0.1$MEAH^+$. The synthesis steps of KTF:*y*$MEAH^+$ (y = 0.05-0.25) is the same as that of KTF:0.1$TEAH^+$.

1.2.6 K_2TiF_6:0.1$HO(CH_2)_2NH_3^+$,$x$$Mn^{4+}$ (KTF:0.1$MEAH^+$,$x$$Mn^{4+}$)

Firstly, 15 ml HF (40%) and 2.5 g KF•$2H_2O$ were weighed and added to a plastic beaker and stirred with a magnetic stirrer until KF•$2H_2O$ was completely dissolved. Then 1.5 mmol (0.37 g) K_2MnF_6 was added to the beaker and stirred for 30 min, and 23.5 mmol (5.74 g) KTF:0.1$MEAH^+$ powder (x = molar ratio of Mn/(Mn+Ti) = 0.06) was added to the beaker and stirred for 30 min. Finally, the mixture was allowed to stand for 24 h, washed several times with acetone and dried at 70 °C for 3 h to obtain sample (ii) KTF:0.1$MEAH^+$,0.06Mn^{4+} (KTF:$MEAH^+$,Mn^{4+}). KTF:0.1$MEAH^+$,$x$$Mn^{4+}$ (x = 0.01-0.12) samples were synthesized in the same way as KTF:$MEAH^+$,Mn^{4+}.

1.2.7 K_2TiF_6:$y$$HO(CH_2)_2NH_3^+$,0.06$Mn^{4+}$ (KTF:$y$$MEAH^+$,0.06$Mn^{4+}$)

Firstly, 15 ml HF (40%) and 2.5 g KF•$2H_2O$ were weighed and added to a plastic beaker and stirred with a magnetic stirrer until KF•$2H_2O$ was completely dissolved. Then 1.5 mmol (0.37 g) K_2MnF_6 was added to the beaker and stirred for 30 min, and 23.5 mmol (5.74 g) KTF:0.1$MEAH^+$ powder (y = molar ratio of MEA / Ti = 0.1) was added to the beaker and stirred for 30 min. Finally, the mixture was allowed to stand for 24 h, washed several times with acetone and dried at 70 °C for 3 h to obtain KTF:0.1$MEAH^+$,0.06Mn^{4+}. KTF:$y$$MEAH^+$,0.06$Mn^{4+}$ (y = 0.05-0.25) samples were synthesized in the same way as KTF:0.1$MEAH^+$,0.06Mn^{4+}.

1.2.8 Assembly of Prototype WLEDs.

Mix YAG:Ce^{3+}, KTF:$MEAH^+$,Mn^{4+} and epoxy resin (the mass ratio of the three is 1.0:5.0:16) and the mixture is coated on the surface of InGaN chips to obtain prototypes of WLEDs.

2. Ninhydrin method detection

Fig. S1 Photos of the reaction of KTF (left) and KTF:0.1MEA (right) with ninhydrin in natural light.

3. Theoretical calculation

3.1 The internal quantum yield

The internal quantum yield of sample is calculated based on Eq. (S1).[24–26]

$$QY_i = \frac{\int L_{emission}}{\int E_{blank} - \int E_{sample}} \quad (S1)$$

Where $L_{emission}$ is the emission spectrum of the sample, E_{blank} and E_{sample} are the spectra of excitation light without and with samples in the integrating sphere, respectively.

3.2. Color purity

The color purity of sample is calculated based on Eq. (S2).[27–29]

$$C_p = \frac{\sqrt{(x - x_i)^2 + (y - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100\% \quad (S2)$$

(x, y) is the chromaticity coordinate of the sample, (x_i, y_i) is the CIE value (0.33, 0.33) of the equal energy light source, (x_d, y_d) is the color coordinate corresponding to the main wavelength of the light source (the chromaticity excited by 467 nm light) The coordinates are: $x_d = 0.1314$, $y_d = 0.0459$).

3.3. Critical distance (R_c)

The critical distance (R_c) between Mn^{4+} ions is determined by using Eq. (S3).[30]

$$R_c \approx 2\left[\frac{3V}{4\pi x_c N}\right]^{1/3} \quad \text{(S3)}$$

Here, V, x_c and N are the unit cell volume of the sample, the critical concentration of Mn^{4+} and the number of sites that activators can substitute per unit, respectively.

3.4. Correlation type of multipolar interaction

The correlation type of multipolar interaction between Mn^{4+} among KTF:0.1MEA,$x$$Mn^{4+}$ using Eq. (S4).[30,31]

$$\frac{I}{x} = k\left[1 + \beta(x)^{\theta/3}\right]^{-1} \quad \text{(S4)}$$

Where I is the PL intensity of the sample and x is the Mn^{4+} concentration greater than x_c. β and k are constants for the same excitation conditions. When θ is equal to 6, 8 and 10, it corresponds to the interaction mechanism of dipole-dipole, dipole-quadrupole and quadrupole-quadrupole, respectively.

3.5. Chromaticity shift

The chromaticity shift (ΔE) at different temperatures was calculated using Eq. (S5).[39,40]

$$\Delta E = \sqrt{(u_t^{'} - u_0^{'})^2 + (v_t^{'} - v_0^{'})^2 + (w_t^{'} + w_0^{'})^2} \quad \text{(S5)}$$

Where $u' = 4x/(3 - 2x + 12y)$, $v' = 9y/(3 - 2x + 12y)$ and $w' = 1 - u' - v'$. x and y are the chromaticity coordinates, v' and u' are the chromaticity coordinates in the $u' \cdot v'$ uniform color space, and 0 and t are room temperature and a given temperature, respectively.

3.6. Activation energy (E_a)

The Eq. (S6) is used to calculate E_a of samples (i)-(iii). Eq. (S6) can be transformed into Eq. (S7), and E_a can be obtained from the slope in Eq. (S7).[41,42]

$$I_T = \frac{I_0}{1 + Aexp(-\frac{E_a}{k_B T})} \quad \text{(S6)}$$

$$Ln\left(\frac{I_0}{I_T} - 1\right) = LnA - \frac{E_a}{k_B T} \quad \text{(S7)}$$

Among them, I_0 and I_T are the initial emission intensity and the emission intensity at a given temperature, respectively. A and k_B are the constant and Boltzmann's constant (8.617×10^{-5} eV/K), respectively.