A low-temperature co-precipitation approach to synthesize fluoride phosphors \( K_2MF_6: Mn^{4+} \) (\( M = Ge, Si \)) for white LED applications†

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1. Introduction

To fabricate warm white light-emitting diodes (WLEDs) with a higher color-rendering index (CRI, \( R_\text{a} > 80 \)), rare-earth activated nitride red phosphors, such as \( \text{MAlSiN}_2: \text{Eu}^{2+} \) (\( M = \text{Ca and Sr} \)) and \( \text{M}_4\text{Si}_5\text{N}_8: \text{Eu}^{2+} \) (\( M = \text{Ca, Sr, and Ba} \)), are commercially added due to their sufficient chemical durability and efficient luminescent properties.† But these phosphors suffer from disadvantages as follows: (1) demanding synthesis conditions for isolating from air and moisture increase the production cost; (2) very broad emission spectrum (full width at half maximum \( \sim 80 \text{ nm} \)) and a large part of the spectrum beyond 650 nm reduces the luminous efficiency of radiation. Hence, alternative red phosphors with high luminescence efficiency from 600 nm to 650 nm, good thermal stability and low production cost should be explored.

Mn\(^{4+}\) (electronic configuration, 3d\(^{5}\)) exhibits sharp emission lines at 600–680 nm because of its distinctive electronic structure. In contrast to the inner 4f \( \rightarrow \) 4f forbidden transition of Eu\(^{3+}\), the outer 3d \( \rightarrow \) 3d transition of Mn\(^{4+}\) is sensitive to local crystal field environments in the host and can be tuned by various substitutions.\(^{12}\) Studies have focused on the preparation and optical properties of Mn\(^{4+}\) activated fluoride phosphors. Adachi \textit{et al.} synthesized a series of Mn\(^{4+}\) activated red fluoride phosphors \( \text{A}_2\text{XF}_6: \text{Mn}^{4+} \) (\( A = \text{K, Na, Cs or NH}_4; \text{X} = \text{Si, Ge, Zr or Ti} \)) and \( \text{BSiF}_6: \text{Mn}^{4+} \) (\( B = \text{Ba or Zn} \)) by wet-chemical etching of silicon wafers. However, this method was inappropriate for quantifiable production because of the high cost of metal wafers and low luminescence efficiency caused by difficulty of controlling the valence state of Mn during synthesis.\(^{13-17}\) The crystal structure of the host and the optical properties of Mn\(^{4+}\) emitters in fluoride phosphors remain unclear.\(^{13-19}\) Hence, the structure–luminescence relationship should be analyzed to properly tune the optical properties of Mn\(^{4+}\) activated fluoride phosphors and meet the requirements of red phosphor. The characteristics and drawbacks of \( K_2\text{GeF}_6: \text{Mn}^{4+} \) and other red phosphors are compared differently in Table S1.† It points on how \( K_2\text{GeF}_6: \text{Mn}^{4+} \) overcomes the drawbacks that other red phosphors have.
In this study, we used the chemical co-precipitation method to synthesize $K_2\text{GeF}_6\text{Mn}^{4+}$ with high purity and good crystallinity without significant defects. The prepared yellowish $K_2\text{GeF}_6\text{Mn}^{4+}$ powders exhibited an efficient emission intensity, high color purity and excellent thermal stability; these substances could be used in commercial applications. As the germanium oxide is easily dissolved in concentrated HF solution, the novel chemical co-precipitation method was operated at room temperature and suitable for quantifiable production because of its high yield, good repeatability and low cost. Particularly, in order to analyze the effects of the host crystal structure on the optical properties of Mn$^{4+}$ emitters, the crystal field and 

Temperature can tune the emission intensity of $K_2(Ge/Si)F_6$; precipitated by slowly adding H$_2$O$_2$. A proposed, and the synthesis temperature was not higher than 55 °C to avoid Mn$^{4+}$ reduction. The specific operation route is shown in the ESI.† 

The valence states of Mn ($2^+$, $3^+$, $4^+$, $6^+$ and $7^+$) are sensitive to the synthesis temperature. Hence, the main difficulty lies in controlling the Mn valence state for synthesizing Mn$^{4+}$ activated fluoride compounds. Thus a two-step strategy of synthesizing $K_2\text{MnF}_6$ initially and then precipitating $K_2(\text{Ge/Si})\text{F}_6\text{Mn}^{4+}$ was proposed, and the synthesis temperature was not higher than 55 °C to avoid Mn$^{4+}$ reduction. The specific operation route is shown in the ESI.† 

The extended X-ray absorption fine structure (EXAFS) analysis were used to probe the optical features of $K_2\text{GeF}_6\text{Mn}^{4+}$ and $K_2\text{SiF}_6\text{Mn}^{4+}$. The synthesis temperature for $K_2\text{GeF}_6\text{Mn}^{4+}$ and $K_2\text{SiF}_6\text{Mn}^{4+}$ red phosphors by synchronously controlling the morphology and valence state of Mn. The optimal synthesis temperature for $K_2\text{GeF}_6\text{Mn}^{4+}$ and $K_2\text{SiF}_6\text{Mn}^{4+}$ red phosphors are 25 °C and 52 °C, respectively; these phosphors were used to investigate the structural and optical properties in this study. The two-step chemical co-precipitation strategy to synthesize $K_2\text{GeF}_6\text{Mn}^{4+}$ red phosphor exhibits the following advantages: 

1. The optimal synthesis temperature is room temperature, which can effectively reduce the volatilization of HF; 
2. The amount of HF consumed to synthesize $K_2\text{GeF}_6\text{Mn}^{4+}$ red phosphor is half of that used to synthesize $K_2\text{SiF}_6\text{Mn}^{4+}$, which is safe and environmentally friendly; 
3. $K_2\text{GeF}_6\text{Mn}^{4+}$ red phosphor synthesized by a two-step chemical co-precipitation method at room temperature exhibits efficient emission intensity and high thermal stability, which are beneficial to commercial applications.

2. Experimental

A two-step chemical co-precipitation method was used to synthesize $K_2(\text{Ge/Si})\text{F}_6\text{Mn}^{4+}$ red phosphors by initially synthesizing $K_2\text{MnF}_6$ and then precipitating $K_2(\text{Ge/Si})\text{F}_6\text{Mn}^{4+}$.

1) Synthesis of $K_2\text{MnF}_6$

High-purity KMnO$_4$ and KHF$_2$ with a mass ratio of 1 : 20 were dissolved in aqueous HF (48%) solution. The mixed solution was stirred and cooled for 0.5 h. The yellow powder $K_2\text{MnF}_6$ was precipitated by slowly adding H$_2$O$_2$. After fast filtering and washing by acetone, the yellow powder was oven-dried for 2 h.

2) Synthesis of $K_2(\text{Ge/Si})\text{F}_6\text{Mn}^{4+}$

GeO$_2$ (2.78 g) and KF (4.65 g) were dissolved in 15 mL HF (48%) aqueous solution at room temperature. After adding 0.2 g of $K_2\text{MnF}_6$ powders in GeO$_2$–HF aqueous solution, the mixed solution was stirred at room temperature or in a water bath with a fixed temperature between 0 °C and 60 °C. The KF–HF solution was added dropwise to the brown GeO$_2$–HF–$K_2\text{MnF}_6$ solution to precipitate a yellow powder at the bottom of the container. Accordingly, the color of the mixture solution changed from brown to almost colorless. After pouring out the supernatant and washing thrice with ethanol, the yellow precipitate was oven-dried for 2 h. However, for the synthesis of $K_2\text{SiO}_{0.95}\text{F}_6\text{Mn}^{4+}$, 1.60 g SiO$_2$ was dissolved in 35 mL HF (48%) aqueous solution in a bath water at 70 °C. Other procedures were similar to the synthesis of $K_2\text{GeF}_{0.95}\text{F}_6\text{Mn}^{4+}$.

3) Structural and optical characterization

Synchrotron X-ray diffraction (XRD) patterns of the samples were collected with a Debye–Scherrer camera installed at the BL01C2 beamline of the National Synchrotron Radiation Research Center (NSRRC, Taiwan) with 0.774907 A wavelength. General Structure Analysis System software was used to analyse the X-ray Rietveld profile refinements of the structural modes. The extended X-ray absorption fine structure spectroscopy (EXAFS) results of Ge K-edge and Si K-edge were obtained at the BL01C and BL16A beamline stations of NSRRC, respectively. The morphologies of the samples were characterized using a scanning electron microscope (SEM, JSM-6700F). High-resolution transmission electron microscopy and selected area electron diffraction images were obtained using a JEOL JEM-2011 microscope operating at 200 kV. The RT excitation and emission spectra were measured using a FluoroMax-3 spectrophotometer equipped with a 150 W Xe lamp. For temperature-dependent experiments at 80–300 K, the samples were placed in a small hold, the temperature of which was controlled by a liquid nitrogen cooling device. Light was radiated using a Hamamatsu R928 photo-multiplier tube. The THMS-600 heating device was also used to study thermal quenching above 300 K.

3. Results and discussion

Fig. 1(a) and (b) respectively show the X-ray Rietveld refinement results and the crystal structure of $K_2\text{GeF}_6\text{Mn}^{4+}$. Fig. S4† illustrates the related structural results of $K_2\text{SiF}_6\text{Mn}^{4+}$. Yellowish $K_2\text{GeF}_6\text{Mn}^{4+}$ powders yield bright red emission upon excitation of 460 nm light, indicating that Mn$^{4+}$ successfully doped into the crystal lattice of $K_2\text{GeF}_6$. The diffraction peaks of $K_2\text{GeF}_6\text{Mn}^{4+}$ phosphor can be indexed to the hexagonal $P\overline{3}m1$ space group with lattice parameters of $a = b = 5.63171$ (6) A, $c = 4.66751$ (6) A, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ and $V = 128.2027$ (20) A$^3$ (JCPDS no. 73-1531). No traces of residual $K_2\text{MnF}_6$ and other impurities are observed. The crystal structure (Fig. 1(b)) shows that each Ge$^{4+}$ is surrounded by 6 F$^-$ to form a regular GeF$_6^{2-}$ octahedron. K$^+$ is at the center of 12 neighbouring F$^-$ . The prepared $K_2\text{SiF}_6\text{Mn}^{4+}$ powders show a lighter color than $K_2\text{GeF}_6\text{Mn}^{4+}$, and emit bright red light under excitation of...
460 nm light. The $K_2SiF_6: Mn^{4+}$ phosphor exhibits a high purity and belongs to the cubic $Fm3m$ space group with lattice parameters of $a = b = c = 8.13107 \text{ Å}$, $\alpha = \beta = \gamma = 90^\circ$ and $V = 537.579 (8) \text{ Å}^3$ (JCPDS no. 37-1155; Fig. S4†). $Si^{4+}$ resides in the vertex and face-centered position of the cubic unit cell; and $4K^+$ ions are uniformly distributed inside the cube. Each $Si^{4+}$ is surrounded by 6 $F^-$ to form a regular $SiF_6^{2-}$ octahedron. Furthermore, central $Ge^{4+}$ and $Si^{4+}$ possess different coordination environments as $GeF_6^{2-}$ and $SiF_6^{2-}$ octahedrons lie in various crystal structures. Measurements of the extended X-ray absorption fine structure (EXAFS) associated with Fourier-transform fitting were used to analyze the coordination environments of $Ge^{4+}$ and $Si^{4+}$. Fig. 1(c) suggests that the bond length between $Ge^{4+}$ and ligand $F^-$ ions (1.81 Å) is longer than that between $Si^{4+}$ and $F^-$ ions (1.66 Å). The differences between $K_2GeF_6: Mn^{4+}$ and $K_2SiF_6: Mn^{4+}$ phosphors in a coordination environment and lattice symmetry of the host structure significantly influence their optical properties.

The microstructures of $K_2GeF_6: Mn^{4+}$ were examined using scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). SEM images indicate that the $K_2GeF_6: Mn^{4+}$ powders show a hexagonal shape, and their sizes range from 20 μm to 50 μm. By contrast, $K_2SiF_6: Mn^{4+}$ powders (Fig. S4(c)†) are octahedral in shape and the particle sizes are in the range of 10–30 μm. Typical HRTEM images reveal a very fine lattice arrangement of $K_2GeF_6: Mn^{4+}$, indicating a single crystal structure with high crystallinity and low structural defects. The selected area electron diffraction image (SAED; inset Fig. 2(b)) exhibits specific shell-shaped-pattern spots corresponding to the [111] zone axis of the hexagonal $P3m1$ space group. The crystal lattice spacing of the (220) plane is about 0.24 nm, which is consistent with the XRD pattern spots corresponding to the [111] zone axis of the cubic unit cell. 

Fig. 2 (a) SEM images and (b) HRTEM images of $K_2GeF_6: Mn^{4+}$ phosphor; (inset) SAED pattern along the [111] zone axis. (c) Element mapping images of Ge, K, F, and Mn for $K_2GeF_6: Mn^{4+}$. All elements show uniform distributions in the image contours, and the shapes of mapping images match well with the HRTEM images.

Fig. 3(a) illustrates the excitation and emission spectra of $K_2GeF_6: Mn^{4+}$ and $K_2SiF_6: Mn^{4+}$ red phosphors measured at room temperature. Consistent with the reported results of other $Mn^{4+}$ activated fluoride compounds, there are two broad excitation bands located in the range of 320–500 nm, corresponding to the spin-allowed transitions of $4A_2g \rightarrow 4T_{1g}$ and $4A_2g \rightarrow 4T_{2g}$, respectively. The sharp red emission lines in the range of 600–650 nm originated from the spin-forbidden $3E_g \rightarrow 3A_{2g}$ transition. Different from the $4A_2g \rightarrow 4T_{1g}$ transition spectra, the $4A_2g \rightarrow 4T_{2g}$ transition of $K_2GeF_6: Mn^{4+}$ and $K_2SiF_6: Mn^{4+}$ red phosphors show several occasional sharp peaks that are attributed to the asymmetric vibronic progression of the $MnF_6$ octahedron supposed on the electronic transition. More importantly, the excitation and emission spectra of $K_2GeF_6: Mn^{4+}$ exhibit a red shift compared to $K_2SiF_6: Mn^{4+}$.

To analyze the red shift behaviour of $K_2GeF_6: Mn^{4+}$, crystal field calculations of the $Mn^{4+}$ energy levels in $K_2GeF_6$ and $K_2SiF_6$ were obtained by diagonalizing the following crystal field Hamiltonian (ESI†). The calculated energy levels (Table 1) conform the red shift of $K_2GeF_6: Mn^{4+}$ phosphor. All the orbital triplets in $K_2GeF_6$ are split into singlets and doublets, as it should be in a hexagonal crystal field. While all orbital triplets are not split in cubic $K_2SiF_6$ since the octahedral symmetry is preserved at the Si position. The first explanation for the red shift is that the electronic density in $K_2GeF_6$ is higher than it is in $K_2SiF_6$. It results in red-shifted energy levels and excitation peaks as shown in Table 1. Ab initio calculations have been indispensably used to assess the perspectives of material applications and limitations. We also used the CASTEP module of Materials Studio package. Diagrams of the partial density of states (DOS; Fig. 3(b)) allow the identification of the lowest
K2GeF6 is smaller than that in K2SiF6, which contributes to the partial DOS diagrams for K2GeF6.

![Fig. 3](image.png)

Table 1: Calculated and experimental energy levels (in cm⁻¹) for Mn⁴⁺ in K₂GeF₆ and K₂SiF₆. The orbital doublet states are denoted with an asterisk. The Racah parameters are also given.

<table>
<thead>
<tr>
<th>Oₐ group</th>
<th>K₂GeF₆ (B = 590; C = 3831)</th>
<th>K₂SiF₆ (B = 605; C = 3806)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁₁</td>
<td>16050</td>
<td>16050</td>
</tr>
<tr>
<td>E国务 (E)</td>
<td>16531</td>
<td></td>
</tr>
<tr>
<td>T₂₁</td>
<td>21545</td>
<td>21598</td>
</tr>
<tr>
<td>T₂₃</td>
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<td>24488</td>
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<td>T₄₃</td>
<td>28808</td>
<td>28922</td>
</tr>
<tr>
<td>T₄₅</td>
<td>45415</td>
<td>45723</td>
</tr>
</tbody>
</table>

Electronic states in the K₂GeF₆ conduction band as those arising from the mixture of the K and Ge 4s states. The F 2p states, which are dominant in the valence band of both crystals, make a minor contribution to the conduction band due to the hybridization effects. Very sharp (strongly localized) 3s and 3p electronic states of K and 2s states of F form narrow electronic bands at high energies. The effective Mulliken charges for all ions were calculated from the generalized gradient approximation (GGA) and local density approximation (LDA; Table S6†). The absolute value of the effective fluorine charge in K₂GeF₆ is smaller than that in K₂SiF₆, which contributes to the weak crystal field in the former host and strong one in the latter host. Therefore, the red shifts of all K₂GeF₆:Mn⁴⁺ spectral bands are consistently explained from the results of ab initio calculations.

Except for the red shift, another interesting phenomenon is also found for K₂GeF₆:Mn⁴⁺ red phosphor: broader excitation and emission bands compared with K₂SiF₆:Mn⁴⁺. The peak positions are dependent on the coordination environments of the MnF₆²⁻ octahedron, while the shape of emission spectra is associated with the crystal structure of the host. Mn⁴⁺ ions in the K₂SiF₆ host with the P₃m₁ space group have Oₙh symmetry, whereas the site symmetry of Mn⁴⁺ ions in the K₂GeF₆ host with the P₃m₁ space group reduces to D₃h. The octahedral symmetry of Oₙh exhibits 6 fundamental internal vibronic modes ν₁ (A₁g), ν₂ (Eₕ), ν₃ (T₁u), ν₄ (T₂u), ν₅ (T₃u) and ν₆ (T₄u). The ungerade vibrations of ν₃, ν₄ and ν₆ introduce some u characters into the 2Eₕ wave functions and then produce the dipole allowed transition. In D₃h symmetry, the triply degenerate modes of ν₁, ν₄ and ν₆ will split into doubly degenerate and non-degenerate modes as a result of small hexagonal distortion,⁹ which results in stronger vibration transition coupling and broad emission lines.

To further reveal the electronic and vibronic structures of Mn⁴⁺ ions in different hosts, the temperature-dependent photoluminescence (PL) spectra were measured and are shown in Fig. S6†. The integrated area of emission increases gradually between 80 K and 300 K in both K₂GeF₆:Mn⁴⁺ and K₂SiF₆:Mn⁴⁺ systems. The decreasing curve of K₂GeF₆:Mn⁴⁺ is observed at temperatures over 300 K. However, it is interesting that the decreasing curve of K₂SiF₆:Mn⁴⁺ is demonstrated at higher temperatures over 470 K. Both of them have high thermal stability at an LED operation temperature (150 °C), and the intensity of emission is still over 90% of them at room temperature. Fig. 4(a) and S7† respectively show the wavelength position and relative intensity of each emission line obtained at different temperatures for K₂GeF₆:Mn⁴⁺ and K₂SiF₆:Mn⁴⁺ red phosphors. The common feature is that all emission peaks show slight red shift and become broader with increasing temperature, which is reasonable as that the unit cell expands and the vibration modes enhance under heat treatment. K₂GeF₆:Mn⁴⁺ exhibit unique split feature of peaks located at 610.0 nm, 610.3 nm, 635.0 nm and 647.0 nm, corresponding to the anti-Stokes ν₄, ν₆ and Stokes ν₃, ν₅ local vibronic emission peaks. The fundamental lattice modes of the transverse acoustic (TA) are more noticeable for Mn⁴⁺ in the hexagonal K₂GeF₆ host with low crystal symmetry. The temperature-dependent behavior of integrated PL intensity IₚL (Fig. 4(b)) shows a considerable amount of stability for K₂GeF₆:Mn⁴⁺ red phosphor in the temperature range of 120–420 K. The relative IₚL at 420 K is above 96%, which is higher than that of rare-earth doped inorganic phosphors. As the vibronic emissions dominate the PL spectra of Mn⁴⁺ in fluorides, both the emission intensity and emission shape are responsible for the IₚL intensity. With increasing temperature from 80 K to 270 K, the anti-Stokes emissions increase dramatically and all emission lines become broader as a result of the increased absorbed photons and enhanced vibration transition coupling associated with the vibration modes of MnF₆²⁻ octahedron, leading to the slight
increase of $I_{PL}$ intensity. A further increase in the temperature above 300 K will increase the non-radiative transition probability and the $I_{PL}$ intensity shows thermal quenching, which can be fitted by $I/I_0 = [1 + D \exp(-E_a/kT)]^{-1}$, where $I_0$ is the intensity at $T = 0$ K, $D$ and activation energy $E_a$ are refined variables. The activation energies obtained for K$_2$GeF$_6$:Mn$^{4+}$ red phosphor is 0.93 eV, which is 4 times higher than that of nitride compounds (~0.23 eV). Moreover, the external quantum efficiency of K$_2$GeF$_6$:Mn$^{4+}$ is 54% at room temperature. To evaluate the commercial application of the synthesized K$_2$GeF$_6$:Mn$^{4+}$ phosphor, the performances of WLEDs (fabricated with blue InGaN chips, Y$_2$Al$_2$O$_3$:Ce$^{3+}$ yellow phosphor and K$_2$GeF$_6$:Mn$^{4+}$ red phosphor) were examined. Electroluminescence spectra of the WLEDs reconfirm the sharp emission lines of Mn$^{4+}$ in K$_2$GeF$_6$ phosphor. A bright “warm” white light with a CRI of 89 is obtained under a drive current of 15 mA (Fig. 4(c)). The chromaticity coordinates of (0.4016, 0.4495) lie near the black body locus and the color temperature for WLEDs is 3974 K. Both the thermal stability and package results indicate the great potential of K$_2$GeF$_6$:Mn$^{4+}$ as commercial red phosphor in warm WLEDs.

4. Conclusions

In summary, the chemical co-precipitation method was used to synthesize the K$_2$GeF$_6$:Mn$^{4+}$ red phosphor with high purity and good crystallinity without significant defects. This method operated at room temperature was suitable for quantifiable production due to its high yield, good repeatability and low cost. The prepared yellowish K$_2$GeF$_6$:Mn$^{4+}$ powders had great potential as a commercial red phosphor thanks to their efficient emission intensity, high color purity and excellent thermal stability. The structural analysis and theoretical calculations showed that the optical properties of Mn$^{4+}$ activated fluoride phosphors were associated with the coordination environments of the MnF$_6^{2-}$ octahedron. The split feature in K$_2$GeF$_6$:Mn$^{4+}$ was caused by hexagonal distortion in the host. The structure–photoluminescence mechanism was predicted to be general in hexafluoride red phosphors to tune the optical properties through cation substitutions and crystal structure adjustments.

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