Quenching of the red Mn$^{4+}$ luminescence in Mn$^{4+}$-doped fluoride LED phosphors

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Abstract
Red-emitting Mn$^{4+}$-doped fluorides are a promising class of materials to improve the color rendering and luminous efficacy of white light-emitting diodes (w-LEDs). For w-LEDs, the luminescence quenching temperature is very important, but surprisingly no systematic research has been conducted to understand the mechanism for thermal quenching in Mn$^{4+}$-doped fluorides. Furthermore, concentration quenching of the Mn$^{4+}$ luminescence can be an issue but detailed investigations are lacking. In this work, we study thermal quenching and concentration quenching in Mn$^{4+}$-doped fluorides by measuring luminescence spectra and decay curves of K$_2$TiF$_6$:Mn$^{4+}$ between 4 and 600 K and for Mn$^{4+}$ concentrations from 0.01% to 15.7%. Temperature-dependent measurements on K$_2$TiF$_6$:Mn$^{4+}$ and other Mn$^{4+}$-doped phosphors show that quenching occurs through thermally activated crossover between the $^4$T$_2$ excited state and $^4$A$_2$ ground state. The quenching temperature can be optimized by designing host lattices in which Mn$^{4+}$ has a high $^4$T$_2$ state energy. Concentration-dependent studies reveal that concentration quenching effects are limited in K$_2$TiF$_6$:Mn$^{4+}$ up to 5% Mn$^{4+}$. This is important, as high Mn$^{4+}$ concentrations are required for sufficient absorption of blue LED light in the parity-forbidden Mn$^{4+}$ $d$-$d$ transitions. At even higher Mn$^{4+}$ concentrations (>10%), the quantum efficiency decreases, mostly due to direct energy transfer to quenching sites (defects and impurity ions). Optimization of the synthesis to reduce quenchers is crucial for developing more efficient highly absorbing Mn$^{4+}$ phosphors. The present systematic study provides detailed insights into temperature and concentration quenching of Mn$^{4+}$ emission and can be used to realize superior narrow-band red Mn$^{4+}$ phosphors for w-LEDs.

Introduction
White light-emitting diodes (w-LEDs) are the next-generation light sources for display and illumination systems because of their small size, high luminous efficacy, and long operation lifetime. Conventional w-LEDs are composed of blue-emitting (In,Ga)N LEDs and green/yellow-emitting and orange/red-emitting phosphors that convert part of the blue LED emission. Both phosphors are necessary to generate warm white light with a high color rendering index (CRI $>$ 85). The typical red phosphors in w-LEDs are Eu$^{2+}$-doped nitrides (e.g., CaAlSiN$_3$: Eu$^{2+}$), $^{4}$T$_2$-$^4$A$_2$ ground state. These phosphors exhibit high photo-luminescence (PL) quantum efficiencies (QE $>$ 90%), but their use also has a serious drawback. The Eu$^{2+}$ emission band is broad and extends into the deep red spectral region ($\lambda > 650$ nm) where the eye sensitivity is low. This causes the luminous efficacy of the w-LED to drop (reduced lumen/W output). A worldwide search is therefore aimed at finding efficient narrow-band red-emitting phosphors that can be excited by blue light. In this search, Mn$^{4+}$-doped fluoride phosphors, such as K$_2$SiF$_6$:Mn$^{4+}$ and K$_2$TiF$_6$:Mn$^{4+}$, have recently attracted considerable attention. Under blue light excitation, Mn$^{4+}$-doped fluorides show narrow red line emission ($\lambda_{\text{max}} \sim 630$ nm) with high luminescence QEs. Furthermore, they are prepared through low-cost, simple wet-chemical synthesis at room temperature. These aspects make Mn$^{4+}$-doped fluorides very promising red-emitting phosphors for developing energy-efficient high color-rendering w-LED systems.
The application of Mn$^{4+}$-doped fluoride phosphors in w-LEDs may, however, be hampered by thermal quenching of the Mn$^{4+}$ luminescence. Thermal quenching of the phosphor luminescence is a serious issue, as it affects both the efficacy and color stability of the w-LED. In high-power w-LEDs, the temperature of the on-chip phosphor layer easily reaches 450 K. At these elevated temperatures, thermal quenching occurs for Mn$^{4+}$-doped fluorides. The luminescence quenching temperature $T_{\text{Quench}}$ is typically between 400 and 500 K$^{15,18,19}$. Although the temperature dependence of the emission intensity has been measured for many Mn$^{4+}$-doped fluorides, the understanding of the thermal quenching behavior is still limited. Most studies do not explain which process quenches the Mn$^{4+}$ luminescence$^{13,20–23}$. Moreover, the few reports that do propose a quenching mechanism disagree. Paulusz$^{15}$ states that the luminescence of Mn$^{4+}$-doped fluorides is quenched by thermally activated crossing of the Mn$^{4+}$ $^4T_2$ excited state and $^4A_2$ ground state. In contrast, Dorenbos$^{24}$ finds a relation between the quenching temperature and the energy of the $F^–\rightarrow$ Mn$^{4+}$ charge-transfer (CT) state and therefore suggests that quenching involves crossover between the CT state and $^4A_2$ ground state. This CT state crossover mechanism was also used by Blasse and our group to explain thermal quenching in Mn$^{4+}$-doped oxides$^{25–27}$. Finally, other reports claim that the quenching temperature increases if the radius of the cation substituted by Mn$^{4+}$ becomes smaller$^{11,18}$. A better understanding of the thermal quenching behavior is essential for developing Mn$^{4+}$-doped fluoride phosphors with superior quenching temperatures, and thereby improving their potential for application in w-LEDs.

Besides thermal quenching, concentration quenching is an issue for the application of Mn$^{4+}$-doped fluorides in w-LEDs. As the Mn$^{4+}$ $d–d$ transitions are parity-forbidden, high Mn$^{4+}$ doping concentrations (e.g., 5 mol%) are required for sufficient absorption of the blue LED light$^{12}$. At high dopant concentrations, energy migration among the Mn$^{4+}$ ions can result in concentration quenching$^{26,28}$, as is illustrated in Fig. 1. If the distance between the Mn$^{4+}$ ions is small, excitation energy may efficiently migrate from one Mn$^{4+}$ ion to another until it reaches a quenching site (defect or impurity site), where the excitation energy is lost non-radiatively (as heat). Studies on concentration quenching in Mn$^{4+}$-doped fluorides are limited. Several works have compared the luminescence properties of fluoride phosphors with varying Mn$^{4+}$ concentrations, but do not measure the actual Mn$^{4+}$ concentration in the phosphors by elemental analysis$^{29–33}$. Determining the Mn$^{4+}$ concentration is crucial, as only a fraction of the Mn$^{4+}$ ions is incorporated during the synthesis$^{19,34}$. Reports that do perform elemental analysis study only a small range of Mn$^{4+}$ doping concentrations and do not provide insight into the role of concentration quenching in Mn$^{4+}$-doped fluorides$^{13,35,36}$. An in-depth investigation of concentration quenching in Mn$^{4+}$-doped fluorides is thus lacking, despite it being very important for the application of Mn$^{4+}$-doped fluorides in w-LEDs.

In this work, we systematically investigate concentration quenching and thermal quenching in Mn$^{4+}$-doped fluorides. The quenching is studied by measuring luminescence spectra and decay curves in the temperature range of 4 to 600 K for K$_2$TiF$_6$:Mn$^{4+}$ phosphors with Mn$^{4+}$ concentrations ranging from 0.01 to 15.7 mol% (actual Mn$^{4+}$ concentration). The temperature-dependent luminescence measurements of K$_2$TiF$_6$:Mn$^{4+}$ and other Mn$^{4+}$-doped phosphors demonstrate that thermal quenching occurs because of thermally activated crossover from the $^4T_2$ excited state to the $^4A_2$ ground state. This insight into the quenching mechanism shows that the Mn$^{4+}$ quenching temperature can be raised by finding fluoride hosts that have an increased Mn$^{4+}$ $^4T_2$ level energy. Concentration studies show that the luminescence QE of K$_2$TiF$_6$:Mn$^{4+}$ is high, ~80%, for doping concentrations up to 5 mol% Mn$^{4+}$. Concentration quenching is limited for these relatively high Mn$^{4+}$ dopant concentrations. At even higher doping concentrations of >10 mol%, the QE of K$_2$TiF$_6$:Mn$^{4+}$ falls below 60%. Luminescence decay curves indicate that the drop in QE can be attributed to an increased probability for direct energy transfer to quenching sites.
(e.g., defects, impurity ions, Mn$^{2+}$ and Mn$^{3+}$), the concentration of which increases with the Mn$^{4+}$ concentration. The present results provide an improved understanding of thermal quenching and concentration quenching in Mn$^{4+}$-doped solids and can be used to develop superior Mn$^{4+}$-doped fluoride phosphors for w-LEDs.

Materials and methods

Synthesis and characterization of K$_2$TiF$_6$:Mn$^{4+}$ phosphors

The K$_2$TiF$_6$:Mn$^{4+}$($x\%$) phosphors were synthesized according to the method of Zhu et al. For the synthesis of K$_2$TiF$_6$:Mn$^{4+}$ (0.8%), 0.0488 g of K$_2$MnF$_6$ (prepared following refs. 37,38) was dissolved in 2.5 mL of a 40 wt% HF solution (Fluka, 40 wt% HF in water). Next, the obtained yellow-brown solution was mixed with 4.5730 g of K$_2$TiF$_6$ (Sigma-Aldrich, p.a.) and then stirred for 1 h at room temperature to form K$_2$TiF$_6$:Mn$^{4+}$ crystals. The K$_2$TiF$_6$:Mn$^{4+}$ phosphor was isolated by decanting the HF solution, washing twice with 15 mL of ethanol and then drying the phosphor for 7 h at 75 °C. The other K$_2$TiF$_6$:Mn$^{4+}$($x\%$) phosphors were prepared following the same procedure but using other amounts of K$_2$MnF$_6$ and K$_2$TiF$_6$ as to obtain different Mn$^{4+}$ doping concentrations.

Powder X-ray diffraction (see Supplementary Figure S1) confirms that the K$_2$TiF$_6$:Mn$^{4+}$($x\%$) phosphors exhibit the hexagonal crystal structure of K$_2$TiF$_6$ up to the highest doping concentration of 15.7% Mn$^{4+}$. Furthermore, no impurities of K$_2$MnF$_6$ or other crystal phases are observed in the diffraction patterns. Scanning electron microscopy (SEM) images show that most K$_2$TiF$_6$:Mn$^{4+}$ phosphor particles are irregularly shaped and have sizes ranging from 1 to 200 µm (see Supplementary Figure S2a). Some particles have a hexagonal shape, in agreement with the hexagonal crystal structure of K$_2$TiF$_6$ (see Supplementary Figure S2b). Energy-dispersive X-ray (EDX) spectra (see Supplementary Figure S2c) confirm that the phosphor particles consist of potassium, titanium, fluorine, and manganese ions. The manganese dopant concentrations in the K$_2$TiF$_6$:Mn$^{4+}$ phosphors were determined with inductively coupled plasma optical emission spectroscopy (ICP-OES). The ICP-OES measurements were performed on a Perkin-Elmer Optima 8300DV spectrometer ($\lambda_{em} = 257.61$ and 259.37 nm). For the ICP-OES analyses, the K$_2$TiF$_6$:Mn$^{4+}$ phosphors were dissolved in aqua regia.

Optical spectroscopy

PL measurements were performed on an Edinburgh Instruments FLS920 fluorescence spectrometer, except for the PL decay measurements between 300 and 600 K (see below). For recording excitation and emission spectra, we used a 450 W Xe lamp as excitation source and a Hamamatsu R928 photomultiplier tube (PMT) with a grating blazed at 500 nm for detection of emission. For PL decay measurements, excitation was done with a tunable optical parametric oscillator (OPO) Optotek Opolette HE 355II laser (pulse width 10 ns, repetition rate 10 Hz) and emission was detected with a Hamamatsu H74220–60 PMT. The PL decay curves between 300 and 600 K were recorded on a different setup, which had an Ekspla NT 342B OPO laser (pulse width 5 ns, repetition rate 10 Hz) as excitation source and a 0.55 m Triax 550 monochromator combined with a Hamamatsu H74220–60 PMT for detection of emission. All PL decay curves were obtained by multi-channel scaling (MCS) with a PicoQuant TimeHarp 260 computer card. The K$_2$TiF$_6$:Mn$^{4+}$ phosphors were cooled down to 4 K with an Oxford Instruments liquid helium flow cryostat. For PL measurements between 300 and 600 K samples were heated in a Linkam THMS600 temperature controlled stage. The PL quantum efficiencies of the phosphors were determined with a calibrated home-built setup, which consisted of a 65 W Xe lamp, excitation monochromator, integrating sphere (Labsphere) and CCD camera (Avantes AvaSpec-2048).

Results and discussion

Luminescence of K$_2$TiF$_6$:Mn$^{4+}$

For our quenching studies, we examine the luminescence of K$_2$TiF$_6$:Mn$^{4+}$ phosphors with a wide range of Mn$^{4+}$ doping concentrations. A photographic image of the K$_2$TiF$_6$:Mn$^{4+}$($x\%$) phosphors is displayed in Fig. 2a. The Mn$^{4+}$ doping concentrations $x$ (molar percentages with respect to Ti$^{4+}$) were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The body color of K$_2$TiF$_6$:Mn$^{4+}$ becomes more yellow with increasing Mn$^{4+}$ concentration as a result of enhanced absorption in the blue. All of the investigated K$_2$TiF$_6$:Mn$^{4+}$ phosphors exhibit bright red Mn$^{4+}$ luminescence under UV photoexcitation.

Figure 2b depicts the Tanabe–Sugano energy level diagram of Mn$^{4+}$ ($3d^5$ electron configuration) in an octahedral crystal field$^{39,40}$. The diagram gives the $d^3$ energy levels as a function of the crystal field splitting $\Delta_0$. Due to its high effective positive charge, Mn$^{4+}$ experiences a strong crystal field and therefore the $2E$ state is the lowest energy excited state. Hence, the emission spectrum of K$_2$TiF$_6$:Mn$^{4+}$ (0.8%) is dominated by narrow red emission lines due to spin- and parity-forbidden $2E \rightarrow 4A_2$ transitions, as can be seen in Fig. 2c. The other K$_2$TiF$_6$:Mn$^{4+}$($x\%$) phosphors exhibit similar emission spectra. As the potential energy curves of the $2E$ and $4A_2$ states are at the same equilibrium position because
the 2E and 4A2 states originate from the same t2g electron configuration.

The 2E → 4A2 emission spectrum consists of a weak zero-phonon line (ZPL) at ~622 nm and more intense anti-Stokes and Stokes vibronic emissions (labeled v3, v4, and v6) on the high and low energy sides of the ZPL, respectively. The ZPL is very weak because Mn4+ is located on a site with inversion symmetry in K2TiF6:Mn4+. Due to the inversion symmetry, there are no odd-parity crystal field components to admix opposite parity states into the 4A2 and 2E states and, as a result, the 2E → 4A2 transition is electric dipole forbidden. The 2E → 4A2 transition can become partly allowed, however, by coupling with asymmetric vibrations that induce odd-parity crystal field components. The most intense lines in Fig. 2c are assigned to 2E → 4A2 transitions coupling with the asymmetric v3, v4, and v6 vibrational modes (phonons) of the MnF206 group. The thermal population of phonons at room temperature allows coupling with v3, v4, and v6 phonon modes in the 2E excited state (giving rise to the anti-Stokes lines), while transitions to these phonon modes in the 4A2 ground state can occur at all temperatures (Stokes lines).

Figure 2d displays the excitation spectrum of the red Mn4+ luminescence from K2TiF6:Mn4+. The two broad excitation bands correspond to spin-allowed 4A2 → 4T1 and 4A2 → 4T2 transitions (violet and blue arrows in Fig. 2b). In addition, some weak peaks are visible around 600 nm. These peaks are assigned to 4A2 → 2E and 4A2 → 2T1 transitions. The 4A2 → 2T1, 2E transitions are spin-forbidden and therefore low in intensity compared to the spin-allowed 4A2 → 2T1, 4T2 transitions.

**Temperature dependence of the Mn4+ luminescence**

To study the thermal quenching of the Mn4+ emission, we measure the PL intensity and Mn4+ emission lifetime of K2TiF6:Mn4+ (0.01%) as a function of temperature between 4 and 600 K. We use a very low Mn4+ doping concentration of 0.01%, as for higher Mn4+ concentrations reabsorption of emission and energy transfer between Mn4+ ions can occur. These processes will influence the temperature dependence of the Mn4+ luminescence spectra and decay curves. As a result, with a high concentration of Mn4+ ions, the observations may not reflect the intrinsic thermal quenching properties of Mn4+. 
Figure 3a shows emission spectra of K$_2$TiF$_6$:Mn$^{4+}$ (0.01%) at various temperatures between 4 and 600 K. At 4 K, the Mn$^{4+}$ $^2\text{E} \rightarrow ^4\text{A}_2$ emission spectrum consists of zero-phonon and Stokes vibronic lines. Upon raising the temperature, phonon modes are thermally populated and anti-Stokes emission lines appear (solid arrow in Fig. 3a). With the appearance of anti-Stokes lines, the relative intensity of the Stokes emission decreases between 4 and 300 K. Above 400 K, the intensities of both the anti-Stokes and Stokes emission lines begin to decrease (dashed arrow in Fig. 3a), which indicates the onset of non-radiative transitions from the $^2\text{E}$ excited state. The luminescence is quenched at 600 K.

The temperature dependence of the Mn$^{4+}$ luminescence from K$_2$TiF$_6$:Mn$^{4+}$ (0.01%) at various temperatures between 0 and 600 K (Fig. 3b). The integrated PL intensity of K$_2$TiF$_6$:Mn$^{4+}$ (0.01%) is scaled to the integrated PL intensity at room temperature ($I_{RT}$). The red and green lines represent fits to Eqs. 6 and 7, respectively.

An alternative method to determine the luminescence quenching temperature is by measuring luminescence decay times. Figure 3c shows a selection of PL decay curves of K$_2$TiF$_6$:Mn$^{4+}$ (0.01%) measured between 4 and 600 K. The decay of the Mn$^{4+}$ emission is single exponential and becomes faster with increasing temperature. The PL decay time is on the order of milliseconds, which is expected as the transition between the $^2\text{E}$ and $^4\text{A}_2$ states is both parity- and spin-forbidden.

The temperature dependence of the Mn$^{4+}$ emission lifetime for K$_2$TiF$_6$:Mn$^{4+}$ (0.01%) (Fig. 3d). The red and green lines represent fits to Eqs. 4 and 8, respectively. The cyan line gives the fit for Eq. 4 (red line) divided by two.
changes with temperature. The \( ^2E \rightarrow ^4A_2 \) emission of K\(_2\)TiF\(_6\):Mn\(^{4+}\) mainly consists of anti-Stokes and Stokes vibronic emissions (Fig. 2c). Their transition probabilities increase with phonon population. The population of phonon modes is given by the phonon occupation number \( n \), which increases with temperature according to \(^{41}\):

\[
n = \frac{1}{\exp(h\nu/k_BT) - 1}
\]

(1)

where \( k_B \) is the Boltzmann constant and \( h\nu \) is the energy of the phonon coupling to the \( ^2E \rightarrow ^4A_2 \) transition. The transition probabilities \( P_R \) of the anti-Stokes and Stokes vibronics scale with \( n \) by:

\[
\text{Anti-Stokes: } P_R(T) = P_R(0)[n] \\
\text{Stokes: } P_R(T) = P_R(0)[n+1]
\]

(2)

(3)

where \( P_R(0) \) is the transition probability at \( T = 0 \) K. As the radiative lifetime \( \tau_R \) is proportional to \( 1/[P_R(\text{anti-Stokes}) + P_R(\text{Stokes})] \), it follows from Eqs. 1–3 that:

\[
\tau_R(T) = \frac{\tau_R(0)}{\coth(h\nu/2k_BT)}
\]

(4)

Here, \( \tau_R(0) \) is the radiative lifetime at \( T = 0 \) K. In Fig. 3d, Eq. 4 (red line) has been plotted for \( \tau_R(0) = 12.3 \) ms and \( h\nu = 216 \) cm\(^{-1}\) (phonon energy of the intense \( v_6 \) mode emission). Equation 4 accurately describes the measured temperature dependence of the Mn\(^{4+}\) emission lifetime up to 375 K, confirming that the decay of the \( ^2E \) state is mainly radiative up to this temperature. The radiative lifetime of the Mn\(^{4+}\) emission shortens with temperature due to thermal population of odd-parity vibrational modes at higher temperatures.

Next, we investigate the increase in PL intensity between 4 and 350 K. The PL intensity \( I_{PL} \) equals the product of the PL QE and number of absorbed photons (as \( I_{PL} \) scales with the number of absorbed photons, the excitation wavelength can have a large influence on the temperature dependence observed for \( I_{PL} \); see Supplementary Information). The PL QE \( \eta \) of K\(_2\)TiF\(_6\):Mn\(^{4+}\) can be expressed as:

\[
\eta = \frac{Y_R}{Y_R + Y_{NR}}
\]

(5)

where \( Y_R \) and \( Y_{NR} \) are the radiative and non-radiative decay rates of the emitting \( ^2E \) state, respectively. The results in Fig. 3d show that the decay of the \( ^2E \) state is mainly radiative up to 375 K, so we can assume that \( Y_{NR} \) is negligible between 0 and 350 K. The value for \( \eta \) is therefore approximated as a constant close to unity between 0 and 350 K. On the other hand, the \( ^4A_2 \rightarrow ^4T_2 \) absorption will change with temperature. Like the \( ^2E \rightarrow ^4A_2 \) transition, the \( ^4A_2 \rightarrow ^4T_2 \) transition is electric dipole (parity) forbidden and gains intensity by coupling with vibrations (for more details on the vibronic structure of the \( ^4A_2 \rightarrow ^4T_2 \) excitation band, see refs. \(^{15,16,44}\)). As a result, the PL intensity \( I_{PL} \) will scale with temperature as \(^{20,41,45}\):

\[
I_{PL}(T) = I(0)\coth\left(\frac{h\nu}{2k_BT}\right)
\]

(6)

with \( I(0) \) being the PL intensity at \( T = 0 \) K. The results in Fig. 3b show that the increase in PL intensity between 4 and 350 K follows the temperature dependence given by Eq. 6. This confirms that the higher PL intensity at 350 K is due to a stronger absorption of excitation light. An increase in PL intensity between 4 and 350 K due to enhanced absorption is observed for all investigated Mn\(^{4+}\) doping concentrations (see Supplementary Information). Although the temperature dependence of the PL intensity follows Eq. 6, there is deviation between the fit of Eq. 6 and the measured data (see red line in Fig. 3b). The model of Eq. 6 is simple and does not take into account the shift and broadening of the \( ^4A_2 \rightarrow ^4T_2 \) absorption band with temperature. Both these effects also influence the temperature dependence of the PL intensity, and this can explain the deviation between the model and the experimental data. Including the effect of a shift and broadening of the \( ^4A_2 \rightarrow ^4T_2 \) band on the absorption strength is complex and will not aid a more accurate determination of \( T_{\eta} \).

Above 400 K the PL intensity of K\(_2\)TiF\(_6\):Mn\(^{4+}\) (0.01\%) begins to decrease due to the onset of non-radiative transitions (Fig. 3a, b). The non-radiative decay probability rapidly increases with temperature above 400 K and as a result the luminescence is quenched, with no emission intensity remaining at 600 K. The quenching temperature \( T_{\eta} \) is determined to be 462 K. The Mn\(^{4+}\) emission lifetime also rapidly decreases once thermal quenching sets in (Fig. 3d). Above 400 K the Mn\(^{4+}\) emission lifetime is shorter than the radiative lifetime \( \tau_R \) predicted by Eq. 4 (red line). The lifetime shortens because of an additional thermally activated non-radiative contribution to the decay of the \( ^2E \) state. From the temperature dependence of the lifetime, \( T_{\eta} \) can be determined by locating the temperature at which the lifetime has decreased to half of its radiative lifetime value. To estimate \( T_{\eta} \), we divide the value from the fit of Eq. 4 for \( \tau_R \) by a factor of 2 (Fig. 3d, cyan line). The cyan line crosses the data points at 457 K. This value for \( T_{\eta} \) is very close to the \( T_{\eta} \) of 462 K obtained from the PL intensity measurements.

Thermal quenching can be described as a thermally activated process with an activation energy \( \Delta E \). The activation energy is obtained by fitting a modified Arrhenius equation to the temperature dependence of the
PL intensity $I_{PL}$ between 350 and 600 K:

$$I_{PL}(T) = \frac{I(0)}{1 + A \times \exp(-\Delta E/k_B T)}$$  \hspace{1cm} (7)

In Eq. 7, $I(0)$ is the maximum PL intensity, $k_B$ is the Boltzmann constant and $A$ is a rate constant for the thermal quenching process. The best fit to Eq. 7 (green line in Fig. 3b) gives an activation energy $\Delta E$ of 9143 cm$^{-1}$ and a rate constant $A$ of $2.5 \times 10^{12}$. We can also determine $\Delta E$ by fitting the temperature dependence of the Mn$^{4+}$ emission lifetime $\tau(T)$ to the following expression:

$$\tau(T) = \frac{\tau_R(T)}{1 + \left(\frac{\tau_R(T)}{\tau_{NR}}\right)\exp(-\Delta E/k_B T)}$$  \hspace{1cm} (8)

Here, $1/\tau_{NR}$ is the non-radiative decay rate and $\tau_R(T)$ is the radiative lifetime as described by Eq. 4 with $\tau_R(0) = 12.3$ ms and $h\nu = 216$ cm$^{-1}$. We fit Eq. 8 to the Mn$^{4+}$ emission lifetimes (green line in Fig. 3d) and find an activation energy $\Delta E$ of 7100 cm$^{-1}$ and a prefactor $1/\tau_{NR}$ of $1.5 \times 10^{12}$ s$^{-1}$. On the basis of the two similar values for $\Delta E$, we conclude that the activation energy of the thermal quenching process is ~8000 cm$^{-1}$. The rate constants $A$ and $1/\tau_{NR}$ should be approximately equal to the vibrational frequencies of the MnF$^2-$ group. The $v_6$ vibrational mode has a frequency of $6.5 \times 10^{12}$ s$^{-1}$, close to the rate constants found by fitting the data to Eqs. 7 and 8. The variation in activation energy values and prefactors can be explained by the fact that thermal quenching is not a simple thermally activated process. Struck and Fonger have shown that the temperature dependence of a non-radiative process is accurately described by considering ground and excited state vibrational wave function overlap. According to the Struck–Fonger model, the non-radiative process occurs through tunneling (crossover) from a vibrational level of the excited state to a high vibrational level of the ground state. The tunneling rate, i.e., the non-radiative decay rate, depends on the wave function overlap of the vibrational levels involved. The tunneling rate will be faster for a larger overlap between the wave functions and when the vibrational levels are in resonance. For the present discussion, analysis of the data using complex models such as the Struck–Fonger model is not relevant, but it is important to realize that the

![Fig. 4 Thermal quenching in Mn$^{4+}$-doped fluorides.](image-url)
Struck–Fonger model gives a more correct description of the actual quenching process.

Thermal quenching in Mn$^{4+}$-doped fluorides

To obtain insight into the thermal quenching of Mn$^{4+}$ luminescence, we will discuss four possible quenching processes: (1) multi-phonon relaxation, (2) thermally activated photoionization, (3) thermally activated crossover via the F$^−$ → Mn$^{4+}$ charge-transfer (CT) state, and (4) thermally activated crossover via the Mn$^{4+}$ $^4T_2$ excited state.

In the configurational coordinate diagram, the parabolas of the Mn$^{4+}$ $^2E$ and $^4A_2$ states do not cross and luminescence quenching by crossover by the $^2E$ to the $^4A_2$ states is not possible (Fig. 4a). The $^4A_2$ ground state may however be reached by multi-phonon relaxation. In Mn$^{4+}$$^+$-doped fluorides more than 30 phonons of ~500 cm$^{-1}$ are needed to bridge the energy gap between the $^2E$ and $^4A_2$ states$^{49}$. For such high numbers of phonons ($p > 30$), it is unrealistic that non-radiative multi-phonon relaxation is responsible for thermal quenching (see Supplementary Information for a more detailed discussion). Alternatively, the thermal quenching can be due to thermally activated photoionization of an electron from the Mn$^{4+}$ $^2E$ state to the fluoride host conduction band. Thermally activated photoionization typically quenches the emission from a luminescent center if the emitting state is close in energy to the host conduction band$^{26,50}$.

In density functional theory (DFT) calculations, large band gaps of around 8 eV have been found for fluoride hosts like K$_2$SiF$_6$ and K$_2$TiF$_6$.$^{51,52}$ It is therefore expected that the Mn$^{4+}$ $^2E$ state is well below the host conduction band levels. Based on this, we conclude that thermal quenching in Mn$^{4+}$$^+$-doped fluorides is not caused by thermally activated photoionization. However, more evidence is necessary to exclude this quenching mechanism. Photoconductivity measurements on Mn$^{4+}$ phosphors at elevated temperatures need to be performed to provide convincing evidence for a possible role of photoionization in the thermal quenching of Mn$^{4+}$ emission.

Thermal quenching in Mn$^{4+}$-doped fluorides has been suggested to occur by thermally activated crossover via the Mn$^{4+}$ $^4T_2$ state or the F$^−$ → Mn$^{4+}$ $^2E$ charge-transfer (CT) state$^{15,24,26}$. Both these states are displaced relative to the potential curve of the $^4A_2$ ground state (Fig. 4a, b). Hence, the $^4T_2$ and CT state parabolas cross the $^4A_2$ ground state parabola. The difference between the potential curve equilibrium positions is given by the offset $\Delta R = R_0 - R_o$. By using the energies of the $^4A_2$ $→ ^2E$, $^4A_2$ $→ ^4T_2$ and $^4A_2$ $→$ CT transitions in K$_2$TiF$_6$:Mn$^{4+}$ (Fig. 2d and ref. 13) and assuming specific offsets $\Delta R$ for the $^4T_2$ and CT states, we can construct the diagrams in Fig. 4a and b, where non-radiative relaxation occurs either via (a) the crossing of the CT and $^4A_2$ states or (b) the crossing of the $^4T_2$ and $^4A_2$ states. The offset of the CT state is typically larger than the offset of the $^4T_2$ state. Note that the diagrams in Fig. 4a and b are schematic configuration coordinate diagrams to illustrate the different quenching mechanisms.

In Fig. 4a, the CT state has a larger offset $\Delta R$ than the $^4T_2$ state, which causes the CT parabola to cross the $^4A_2$ parabola at lower energies than the $^4T_2$ parabola. Thermal activation over the energy barrier $\Delta E$ will allow crossover from the $^2E$ state into the CT state followed by non-radiative relaxation to the ground state via the crossing of the CT and $^4A_2$ parabolas. Alternatively, thermal quenching of the Mn$^{4+}$ luminescence may be due to the mechanism depicted in Fig. 4b. Here, the CT state has a smaller offset $\Delta R$ compared to that shown in Fig. 4a, and its potential curve is therefore at higher energies. In addition, the $^4T_2$ state has a slightly larger offset. As a result, the crossing of the $^4T_2$ and $^4A_2$ parabolas is now at a lower energy and non-radiative relaxation will proceed via the crossing of the $^4T_2$ and $^4A_2$ parabolas.

The activation energies $\Delta E$ in the configuration coordinate diagrams are ~8000 cm$^{-1}$, similar to the $\Delta E$ values obtained from the temperature-dependent measurements. This indicates that both mechanisms in Fig. 4a, b can explain the thermal quenching of Mn$^{4+}$ luminescence. To determine which of these two mechanisms is responsible for the luminescence quenching, we compare the quenching temperature $T_q$ of K$_2$TiF$_6$:Mn$^{4+}$ to the $T_q$ of other Mn$^{4+}$-doped materials. A relation between the quenching temperature and the energy of either the CT or $^4T_2$ state in a variety of hosts will give insight. If quenching occurs by crossover from the CT state to the $^4A_2$ state, $T_q$ will be higher for Mn$^{4+}$-doped solids with higher CT transition energies. In K$_2$TiF$_6$:Mn$^{4+}$ and other Mn$^{4+}$-doped fluorides the F$^−$ → Mn$^{4+}$ CT transition is at ~40,000 cm$^{-1}$.$^{11,15}$ Mn$^{4+}$-doped oxides have lower O$^{2-}$ → Mn$^{4+}$ CT transition energies of 30,000–35,000 cm$^{-1}$ and are therefore expected to have lower $T_q$ values than fluorides if quenching occurs by the mechanism in Fig. 4a.$^{26,27,33,34}$ Some Mn$^{4+}$-doped oxides, however, have much higher quenching temperatures than Mn$^{4+}$-doped fluorides. For example, Mg$_6$GeO$_6$:Mn$^{4+}$, Mg$_{26}$Ge$_{27}$O$_{38}$F$_{16}$:Mn$^{4+}$, and Mg$_6$As$_2$O$_{11}$:Mn$^{3+}$ have a $T_q$ of ~700 K.$^{55–57}$, while K$_2$TiF$_6$:Mn$^{2+}$ and other Mn$^{4+}$-doped fluorides have a $T_q$ of 400–500 K (see also Tables 1 and 2). No correlation is found between the Mn$^{4+}$ luminescence quenching temperature and the energy of the CT transition (see Supplementary Information for an overview and a plot of quenching temperatures and CT energies). From this we conclude that thermal quenching in Mn$^{4+}$-doped fluorides is not caused by thermally activated crossover from the F$^−$ → Mn$^{4+}$ CT state to the $^4A_2$ ground state.
Alternatively, thermal quenching of the Mn$^{4+}$ luminescence can be caused by thermally activated crossover via the Mn$^{4+}$ 4T$_2$ excited state (Fig. 4b). To investigate the validity of this mechanism, we compare the $T_{\text{4T}_2}$ and 4A$_2$ → 4T$_2$ transition energies for K$_2$TiF$_6$:Mn$^{4+}$ and a variety of other Mn$^{4+}$-doped fluorides. From the literature and measurements on Mn$^{4+}$ luminescence we have collected quenching temperatures and luminescence spectra, preferably for systems with low doping concentrations. Figures 2d and 3b show that K$_2$TiF$_6$:Mn$^{4+}$ has a 4A$_2$ → 4T$_2$ energy of 21,459 cm$^{-1}$ (maximum of the excitation band) and a $T_{\text{4T}_2}$ of 462 K. For K$_2$SiF$_6$:Mn$^{4+}$, we measured a 4A$_2$ → 4T$_2$ energy of 22,099 cm$^{-1}$ and a $T_{\text{4T}_2}$ of 518 K (Supplementary Figure S6, K$_2$SiF$_6$:Mn$^{4+}$:BR301-C commercial phosphor from Mitsubishi Chemical, Japan). In Fig. 4c we plot the quenching temperature $T_{\text{4A}_2}$ against the 4A$_2$ → 4T$_2$ energy for K$_2$TiF$_6$:Mn$^{4+}$, K$_2$SiF$_6$:Mn$^{4+}$ and many other Mn$^{4+}$-doped fluoride phosphors reported in the literature (displayed data also listed in Table 1). The data show that the $T_{\text{4A}_2}$ increases with the energy of the 4T$_2$ state. The clear trend shows that the thermal quenching in Mn$^{4+}$-doped fluorides is due to thermally activated crossover from the 4T$_2$ excited state to the 4A$_2$ ground state. Further confirmation for this quenching mechanism is provided by Mn$^{4+}$ spectra measured at elevated temperatures (see Supplementary Information). Supplementary Figure S7 shows emission spectra of K$_2$SiF$_6$:Mn$^{4+}$ at $T = 573$ and 673 K. At 573 K a broad 4T$_2$ → 4A$_2$ emission band is observed, which is almost completely quenched at 673 K. The initial rise of the 4T$_2$ → 4A$_2$ emission at elevated temperatures confirms thermal population of the 4T$_2$ level, which eventually leads to thermal quenching of all Mn$^{4+}$ emission via this state.

To investigate whether thermally activated crossing via the 4T$_2$ state is also responsible for temperature quenching in Mn$^{4+}$-doped oxides, we extend the data set of Fig. 4c with quenching temperatures reported for Mn$^{4+}$-doped oxides. Figure 4d shows the quenching temperature $T_{\text{4A}_2}$ as a function of the 4A$_2$ → 4T$_2$ energy for the Mn$^{4+}$-doped fluorides and oxides listed in Tables 1 and 2. The results show that $T_{\text{4A}_2}$ increases with the energy of the 4A$_2$ → 4T$_2$ transition. This indicates that the Mn$^{4+}$ emission in fluorides and oxides are both quenched due to thermally activated crossover from the 4T$_2$ excited state, and not the CT state as previously suggested in some reports$^{24-27}$. The present results and analysis provide strong evidence that in many Mn$^{4+}$ phosphors the thermal quenching mechanism involves thermally activated crossover via the 4T$_2$ excited state. A contribution from other mechanisms cannot be ruled out and further research, for example, photoconductivity measurements and high pressure studies, can give additional information on the role of alternative quenching mechanisms.

### Table 1 Quenching temperature $T_{\text{4A}_2}$ (K) and 4A$_2$ → 4T$_2$ energy (cm$^{-1}$) for Mn$^{4+}$-doped fluoride materials

| Host lattice | 4A$_2$ → 4T$_2$ energy (cm$^{-1}$) | $T_{\text{4A}_2}$ (K) | References |
|-------------|----------------------------------|----------------------|------------|
| K$_2$TiF$_6$ | 21,459                           | 462                  | This work |
| K$_2$GeF$_6$ | 22,099                           | 518                  | This work |
| K$_2$SiF$_6$ | 22,120                           | 490                  | 15         |
| K$_2$GeO$_3$ | 21,280                           | 470                  | 15         |
| K$_2$GeF$_6$ | 21,190                           | 450                  | 15         |
| K$_2$TiF$_6$ | 21,368                           | 478                  | 13         |
| Na$_2$SiF$_6$ | 21,739                           | 488                  | 21         |
| Rb$_2$SiF$_6$ | 21,739                           | 480                  | 18         |
| Rb$_2$TiF$_6$ | 21,186                           | 450                  | 18         |
| Rb$_2$GeF$_6$ | 21,739                           | 513                  | 60         |
| Cs$_2$GeF$_6$ | 21,277                           | 420                  | 22         |
| Cs$_2$SiF$_6$ | 21,368                           | 430                  | 22         |
| Cs$_2$HfF$_6$ | 20,964                           | 403                  | 44         |
| BaSiF$_6$    | 21,322                           | 430                  | 23         |
| BaSnF$_6$    | 21,008                           | 400                  | 45         |
| BaTiF$_6$    | 21,142                           | 425                  | 61         |

### Table 2 Quenching temperature $T_{\text{4A}_2}$ (K) and 4A$_2$ → 4T$_2$ energy (cm$^{-1}$) for Mn$^{4+}$-doped oxide materials

| Host lattice | 4A$_2$ → 4T$_2$ energy (cm$^{-1}$) | $T_{\text{4A}_2}$ (K) | References |
|-------------|----------------------------------|----------------------|------------|
| Mg$_2$GeO$_3$ | 23,697                           | 730                  | 55         |
| Mg$_2$Ge$_2$Os$_3$F$_{10}$ | 23,923                           | 700                  | 26,55,56   |
| K$_2$GeO$_3$ | 21,739                           | 373                  | 62         |
| K$_2$GeO$_3$ (site 1) | 19,231                           | 160                  | 63         |
| K$_2$GeO$_3$ (site 2) | 21,700                           | 379                  | 63         |
| Rb$_2$GeO$_3$ (site 1) | 19,231                           | 162                  | 63         |
| Rb$_2$GeO$_3$ (site 2) | 20,850                           | 346                  | 63         |
| Y$_2$MgGe$_2$O$_{12}$ | 23,753                           | 850                  | 64         |
| La$_2$GaGe$_2$O$_{16}$ | 21,413                           | 420                  | 65         |
| La$_2$ZnTiO$_6$ | 19,608                           | 230                  | 66         |
| La$_2$MgTiO$_6$ | 20,000                           | 250                  | 66         |
| CaZrO$_3$    | 18,500                           | 300                  | 25,26      |
| Mg$_2$Al$_2$O$_{11}$ | 23,810                           | 680                  | 57         |
| Y$_2$Al$_2$O$_4$ | 20,619                           | 300                  | 67         |
| Y$_3$Al$_5$O$_{12}$ | 20,833                           | 300                  | 68         |
| Sr$_2$Al$_2$O$_{25}$ | 22,222                           | 423                  | 69         |
| SrLaAlO$_4$  | 19,231                           | 300                  | 53         |
| LiGa$_2$O$_6$ | 20,000                           | 350                  | 70         |
As quenching occurs by thermally activated crossover via the $^4T_2$ excited state, the quenching temperature $T_q$ of the Mn$^{4+}$ luminescence is controlled by the energy of the $^4T_2-^4A_2$ state (the dependence of $T_q$ on the energy of the $^4T_2$ state is shown in Fig. 4c,d). In addition, the $T_q$ of the Mn$^{4+}$ luminescence depends on the offset $\Delta R$ between the $^4T_2$ and $^4A_2$ states, as $\Delta R$ also determines where the $^4T_2$ and $^4A_2$ states cross in the configuration coordinate diagram (Fig. 4a,b). The horizontal displacement of the $^4T_2$ parabola will influence the quenching temperature. A variation in $\Delta R$ can explain the spread observed in the data of Fig. 4c and d. To investigate the variation in the offset $\Delta R$ for Mn$^{4+}$-doped fluorides, we compare the bandwidth of the $^4A_2 \rightarrow ^4T_2$ excitation band in K$_2$TiF$_6$:Mn$^{4+}$, K$_2$SiF$_6$:Mn$^{4+}$ and Cs$_2$HfF$_6$:Mn$^{4+}$ (see Supplementary Figure S9). The width of the $^4A_2 \rightarrow ^4T_2$ excitation band is controlled by the displacement of the $^4T_2$ state and therefore gives a good indication of $\Delta R$. Comparison of the $^4A_2 \rightarrow ^4T_2$ bandwidths shows that there is a variation in $\Delta R$ for Mn$^{4+}$-doped fluorides. The variation in $\Delta R$ is small, however, compared to the differences in the $^4T_2$ energy, and no correlation is observed between the spectral width and quenching temperatures. This indicates that the $^4T_2$ level energy has the largest influence on the quenching temperature of Mn$^{4+}$-doped fluorides.

Finally, in view of applications, it is interesting to see how we can control the $^4T_2$ level energy (and thereby $T_q$) through the choice of the host lattice. The energy of the Mn$^{4+}$-$^4T_2$ state depends on the crystal field splitting $\Delta_O$ (Fig. 2b), where $\Delta_O$ is typically larger for shorter Mn–F distances. For Mn$^{4+}$-doped fluorides the luminescence quenching temperature can therefore be raised by selecting host lattices with short Mn–F distances (see Supplementary Figure S10a). This is consistent with findings that $T_q$ decreases as the radius of the Mn$^{4+}$ host cation decreases, as expected based on crystal field theory. If, however, $T_q$ is plotted against the Mn$^{4+}$-ligand...
distance for both Mn$^{4+}$-doped fluorides and Mn$^{3+}$-doped oxides (see Supplementary Figure S10b), no correlation between $T_{1/2}$ and the M$^{4+}$-ligand distance is found. This shows that the crystal field splitting and $^4T_2$ energy give a better indication of the quenching temperature for Mn$^4^+$-doped phosphors.

Concentration quenching

In addition to insight into thermal quenching, concentration quenching in Mn$^{4+}$-doped fluorides is important for application in w-LEDs. The weak parity-forbidden $^4A_2 \rightarrow ^4T_2$ absorption requires that commercial phosphors have high Mn$^{4+}$ concentrations. If there is effective concentration quenching, the PL decay time and QE will decrease when the Mn$^{4+}$ doping concentration is raised\cite{26,28}. We therefore investigate concentration quenching in K$_2$TiF$_6$Mn$^{4+}$ by measuring the PL decay times and QEs of K$_2$TiF$_6$Mn$^{4+}$ phosphors with Mn$^{4+}$ concentrations ranging from 0.01 to 15.7% Mn$^{4+}$.

Figure 5a presents room-temperature PL decay curves of the Mn$^{4+}$ emission from K$_2$TiF$_6$Mn$^{4+}$ with increasing Mn$^{4+}$ doping concentration $x$. It can be seen that the PL decay becomes slightly faster as the Mn$^{4+}$ concentration increases. We analyze the decay dynamics by single exponential fitting of the PL decay curves. The fit for K$_2$TiF$_6$Mn$^{4+}$ (0.8%) is shown in Fig. 5b. The fit residuals (bottom panel) are random and the PL decay thus resembles a single exponential. This indicates that the decay of the $^2E$ state is mainly radiative. Consequently, the K$_2$TiF$_6$Mn$^{4+}$ (0.8%) phosphor has a very high QE of 90%. Figure 5c gives an overview of the fitted decay times (blue squares) and QEs (red dots) of K$_2$TiF$_6$Mn$^{4+}$ with different Mn$^{4+}$ concentrations. The emission lifetime barely shortens if the Mn$^{4+}$ concentration is increased (5.7 ms for 0.01% Mn$^{4+}$ to 5.4 ms for 15.7% Mn$^{4+}$). This suggests that energy migration to quenching sites is inefficient in K$_2$TiF$_6$Mn$^{4+}$. To verify this, we look at the QE values obtained for the K$_2$TiF$_6$Mn$^{4+}$ (x%) phosphors. The QE remains above 80% for Mn$^{4+}$ doping concentrations of 5% or less, which shows that concentration quenching is indeed limited up to a concentration of 5% Mn$^{4+}$ ions. This result is important for applications in w-LEDs, as these high Mn$^{4+}$ doping concentrations (e.g., 5 mol%) are required for sufficient absorption of the blue LED light in the parity-forbidden $d-d$ transitions\cite{12}.

For higher Mn$^{4+}$ concentrations (x > 10%), non-radiative decay from the $^2E$ excited state becomes stronger, however, and as a result the QE of K$_2$TiF$_6$Mn$^{4+}$ falls below 60% (Fig. 5c). The non-radiative decay is also visible in the PL decay curve of K$_2$TiF$_6$Mn$^{4+}$ (15.7%), shown in Fig. 5d. The decay is multi-exponential, which proves that with 15.7% Mn$^{4+}$, the $^2E$ state decays both radiatively and non-radiatively. The faster initial decay indicates that there is enhanced quenching by single-step energy transfer for Mn$^{4+}$ ions close to a quencher. In case of energy migration, a faster decay is also expected for longer times after the excitation pulse. As this is not observed, the contribution of energy migration via many Mn$^{4+}$ ions to quenching sites seems to be small.

To further investigate the role of energy migration in the concentration quenching of the Mn$^{4+}$ emission, we measure a PL decay curve of K$_2$TiF$_6$Mn$^{4+}$ (15.7%) at $T = 4\, K$, which is displayed in Fig. 5e. At $T = 4\, K$ energy migration among the Mn$^{4+}$ ions (blue arrows in Fig. 1) will be hampered, as there is almost no spectral overlap between the Mn$^{4+}$ $^2E \rightarrow ^4A_2$ emission and $^4A_2 \rightarrow ^2E$ excitation lines (see Supplementary Figure S11). Hence, at $4\, K$ non-radiative decay due to energy migration to quenching sites will be suppressed. The Mn$^{4+}$ decay dynamics in Fig. 5e, however, show that the non-radiative decay is not suppressed at $4\, K$. The deviation from single exponential behavior is similar to that at $300\, K$. There is an initial faster decay (single-step energy transfer to quenching sites) followed by an exponential decay with a decay time very close to that measured for Mn$^{4+}$ at low doping concentrations. This suggests that the decrease in QE at higher Mn$^{4+}$ concentrations is not due to energy migration. The absence of strong concentration quenching by energy migration is confirmed by the thermal quenching behavior measured for the different Mn$^{4+}$ concentrations. In Supplementary Figure S4, it can be seen that the luminescence quenching temperature is approximately the same for doping concentrations of 0.01% and 15.7% Mn$^{4+}$, which shows that effects due to thermally activated energy migration (i.e., concentration quenching) are weak. Hence, we conclude that the non-radiative decay at high Mn$^{4+}$ concentrations is not caused by energy migration. Inefficient energy migration can be understood based on the strongly forbidden character of the $^2E \rightarrow ^4A_2$ transition. This allows only Mn$^{4+}$–Mn$^{4+}$ energy transfer via short range exchange interaction (see Supplementary Information for details).

We instead assign the non-radiative decay to direct transfer of excitation energy from Mn$^{4+}$ ions to quenchers (green arrow in Fig. 1). This process can occur at all temperatures and becomes more efficient at higher Mn$^{4+}$ dopant concentrations. With an increasing Mn$^{4+}$ dopant concentration, the stress on the K$_2$TiF$_6$ lattice grows and as a result more crystal defects (i.e., quenchers) may be formed. In addition, Mn in different valence states (Mn$^{2+}$ and Mn$^{3+}$) may be incorporated at higher Mn$^{4+}$ concentrations. Even if a very small fraction of Mn$^{4+}$ ions has a different valence state than Mn$^{4+}$, effective quenching can occur via metal-to-metal charge-transfer states or direct energy transfer. Consequently, the probability for energy transfer to quenchers increases, resulting in faster initial PL decay and lower QEs for K$_2$TiF$_6$Mn$^{4+}$ at high Mn$^{4+}$ dopant concentrations. Optimized synthesis procedures
to reduce quenchers (defects and impurity ions) are thus crucial for obtaining highly luminescent Mn\textsuperscript{4+}-doped fluoride phosphors (see also recent work of Garcia-Santamaría et al.\textsuperscript{59} on concentration quenching in K\textsubscript{2}SiF\textsubscript{6}:Mn\textsuperscript{4+}).

**Conclusions**

Narrow-band red-emitting Mn\textsuperscript{4+} phosphors form an important new class of materials for LED lighting and displays. For these applications, it is important to understand and control the luminescence efficiency. We have therefore investigated quenching of the Mn\textsuperscript{4+} luminescence in Mn\textsuperscript{4+}-doped fluorides by measuring the PL intensity and luminescence lifetimes of K\textsubscript{2}TiF\textsubscript{6}:Mn\textsuperscript{4+} between 4 and 600 K and for Mn\textsuperscript{4+} concentrations from 0.01 to 15.7%. Temperature-dependent measurements of the Mn\textsuperscript{4+} emission intensity and lifetime for K\textsubscript{2}TiF\textsubscript{6}:Mn\textsuperscript{4+} and other Mn\textsuperscript{4+}-doped phosphors show that thermal quenching is caused by thermally activated crossover via the Mn\textsuperscript{4+}↑\textsubscript{4}T\textsubscript{2} excited state. As a result, the quenching temperature is higher in Mn\textsuperscript{4+}-doped materials with higher ↑\textsubscript{T2} state energies. These findings can be used to engineer Mn\textsuperscript{4+}-doped fluoride phosphors with higher quenching temperatures for application in high-power white LEDs.

Furthermore, quantum efficiency and luminescence decay measurements for a wide range of Mn\textsuperscript{4+} doping concentrations show that no concentration quenching occurs up to 5% Mn\textsuperscript{4+} in K\textsubscript{2}TiF\textsubscript{6}:Mn\textsuperscript{4+}. This is important for the application of Mn\textsuperscript{4+}-doped materials in white LEDs, as high Mn\textsuperscript{4+} doping concentrations (e.g., 5 mol\%) are required for sufficient absorption of the blue LED light in the parity-forbidden Mn\textsuperscript{4+} d–d transitions. At very high Mn\textsuperscript{4+} doping concentrations (>10 mol\%) the quantum efficiency of K\textsubscript{2}TiF\textsubscript{6}:Mn\textsuperscript{4+} decreases due to enhanced direct energy transfer from Mn\textsuperscript{4+} to quenching sites. Concentration quenching by Mn\textsuperscript{4+}–Mn\textsuperscript{4+} energy migration is limited. To optimize the efficiency in highly doped Mn\textsuperscript{4+} phosphors, a synthesis procedure aimed at reducing quenching sites (defects, impurity ions, Mn\textsuperscript{2+}, and Mn\textsuperscript{3+}) will be crucial.

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**Supplementary information**

The authors declare that they have no conflict of interest.

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