Red Emitting $K_3(Zr_{1-x}Hf_x)F_7:Mn^{4+}$ Translucent Ceramics for Warm-White LED Applications

Thomas Jansen, Jürgen Gorobez, and Thomas Jüstel

Department of Chemical Engineering, Münster University of Applied Sciences, Stegerwaldstraße 39, 48565 Steinfurt, Germany

Corresponding authors: t.jansen@fh-muenster.de ; tj@fh-muenster.de

Phosphor Global Summit 2018, March 14-15, San Diego, CA, USA

Background

Recently, Mn^{4+} doped alkaline metal fluorometallates have attracted much attention due their blue shifted PL in comparison to Mn^{4+} doped oxides. Particularly, $K_2SiF_6:Mn^{4+}$ and $K_2TiF_6:Mn^{4+}$ have been studied intensively. These material classes emit intense light in the desired red spectral region and thus meet the requirements concerning efficiency and color quality for “future warm white” pcLEDs. Lately, a synthesis method for $K_3ZrF_7:Mn^{4+}$ and its PL properties have been published. They described the luminescence behavior of Mn^{4+} ions in seven-coordination environment within the K_3ZrF_7 host material for the first time [1]. A closer look, however reveals, that the photoluminescence is likely caused by an octahedral coordinated Mn^{4+} center rather than from a seven-coordinated center. To further elucidate the Mn^{4+} luminescence in fluorides with seven-fold coordinated crystallographic sites, we decided to investigate Mn^{4+} activated K_3ZrF_7 and K_2HfF_7 as red emitting component for pcLEDs in details. Additionally, we prepared translucent Mn^{4+} doped fluoride ceramics with enhanced absorption properties for the first time.

Synthesis and Structure

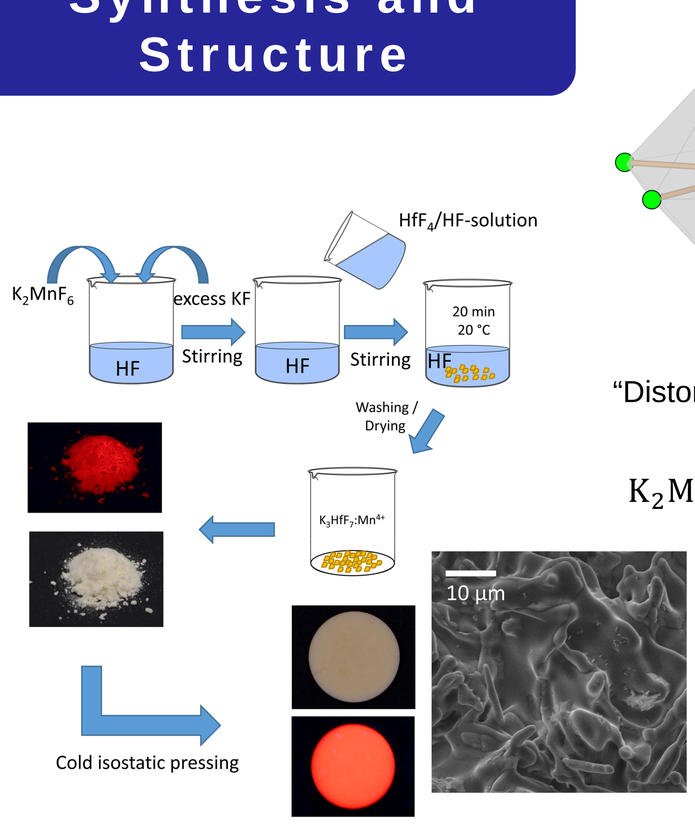
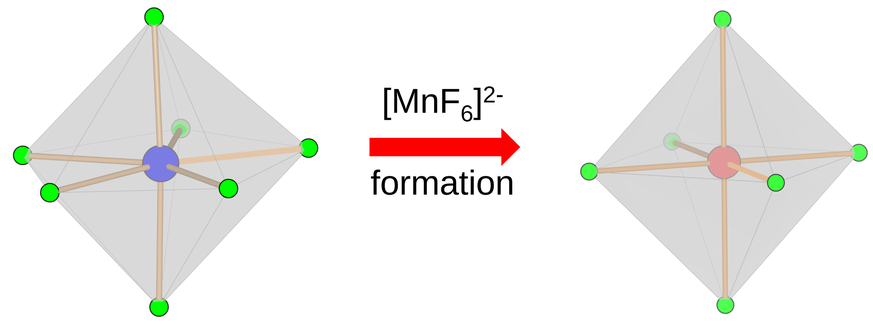


Fig. 1 Sketch of the preparation pathway of $K_3Zr_{1-x}HfF_7:Mn^{4+}$ ceramics.

Fig. 2 Formation of the $[MnF_6]^{2-}$ octahedra in $K_3Zr_{1-x}Hf_xF_7$.



$[MF_7]^{3-}$ (M = Zr,Hf)
“Distorted pentagonal bipyramid”

$[MnF_6]^{3-}$
“Distorted octahedron”

$$K_2MnF_6 \xrightarrow{K_3MF_7\ (M=Zr,Hf)} 2\,K_K^{\times} + Mn_M^{\times} + 6\,F_F^{\times} + V_K' + V_F^{\bullet}$$

Tab. 1 Refined unit cell parameters for powder samples of K_3ZrF_7 and K_3HfF_7

	K_3ZrF_7	K_3HfF_7
Space group	$Fm\bar{3}m$	$Fm\bar{3}m$
$a = b = c$ /Å	8.951(10)	8.9735(5)
$\alpha = \beta = \gamma$ /°	90	90
V /Å^3	717.16	722.58
Zr/Hf site symmetry	C_1	C_1

Results and Discussion

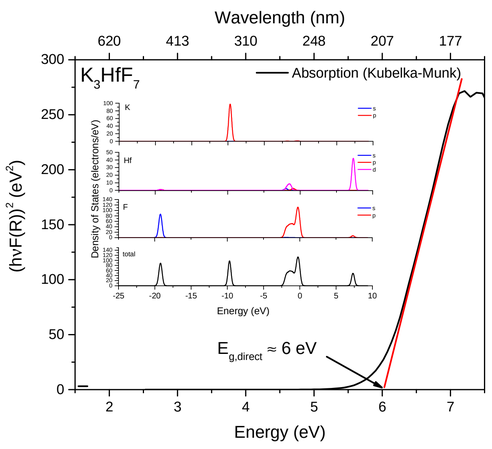


Fig. 3 Tauc plot of undoped K_3HfF_7 (derived from diffuse UV reflectance measurement). The inset shows sx-LDA calculated DOS diagrams (From the top: K, Hf, F partial DOS and total DOS).

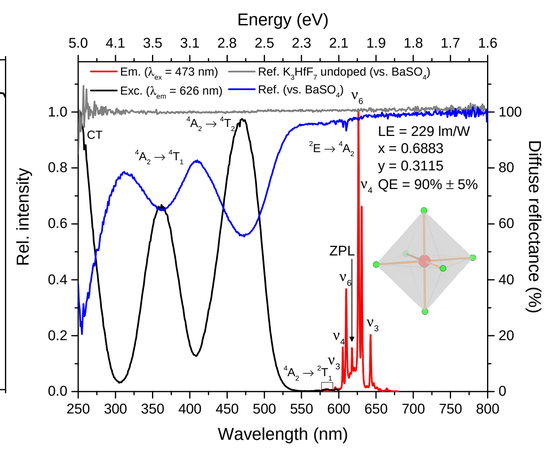


Fig. 4 Excitation, emission, and reflectance spectra of $K_3HfF_7:Mn^{4+}$ (1%) at room temperature.

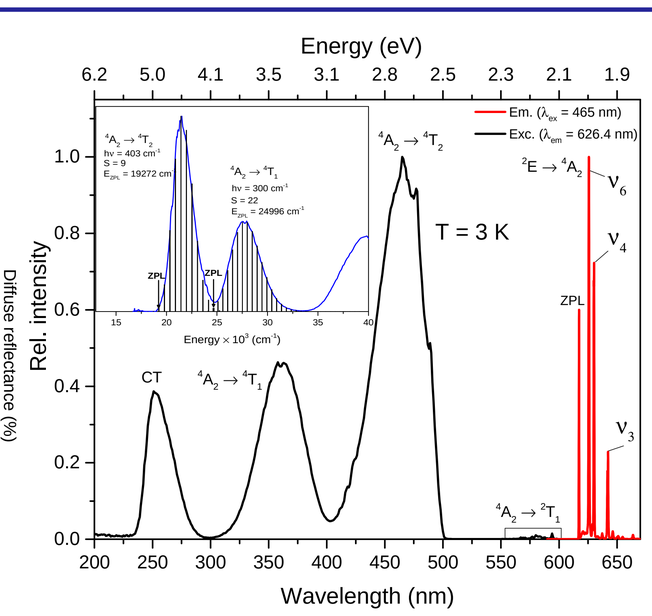


Fig. 5 Excitation and emission spectra of $K_3HfF_7:Mn^{4+}$ (1%) at 3 K. The inset shows the phonon progression of the $^4T_2$ and $^4T_1 \rightarrow {}^4A_2$ excitation bands.

Table 2: Calculated Racah parameter of $K_3HfF_7:Mn^{4+}$

$^4A_2 \rightarrow {}^4T_2$	19272 cm^{-1}
$^4A_2 \rightarrow {}^4T_1$	24996 cm^{-1}
$^2E \rightarrow {}^4A_2$	15964 cm^{-1}
Dq	1927
B	763
C	3435
β‘	1.035

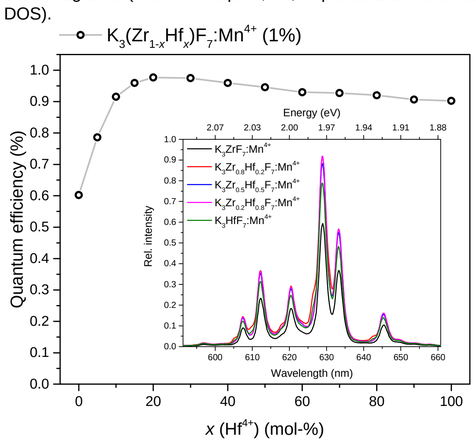


Fig. 6 Quantum efficiencies of the $K_3Zr_{1-x}Hf_xF_7:Mn^{4+}$ (1%). solid solution. The inset shows the relative emission spectra of the $K_3Zr_{1-x}Hf_xF_7:Mn^{4+}$ (1%) samples.

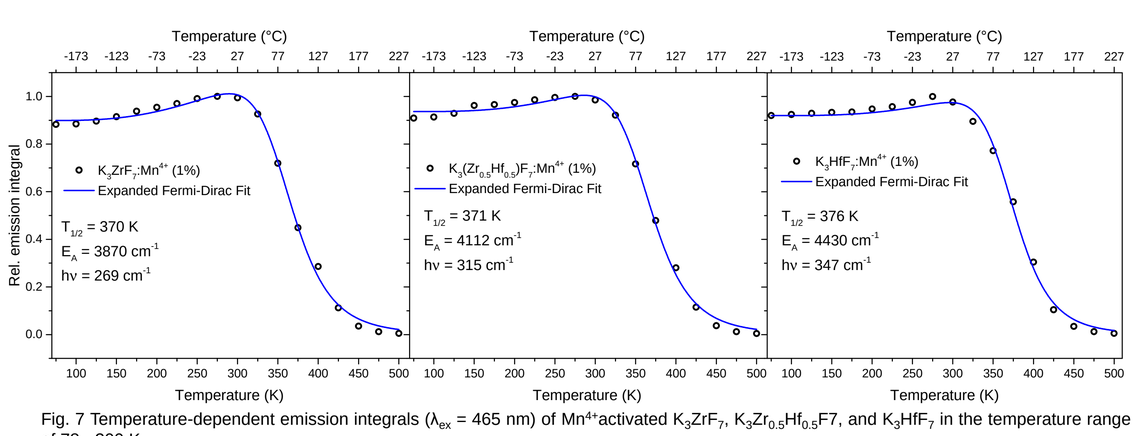


Fig. 7 Temperature-dependent emission integrals (λ_{ex} = 465 nm) of Mn^{4+}activated K_3ZrF_7, $K_3Zr_{0.5}Hf_{0.5}F7$, and K_3HfF_7 in the temperature range of 78 - 300 K.

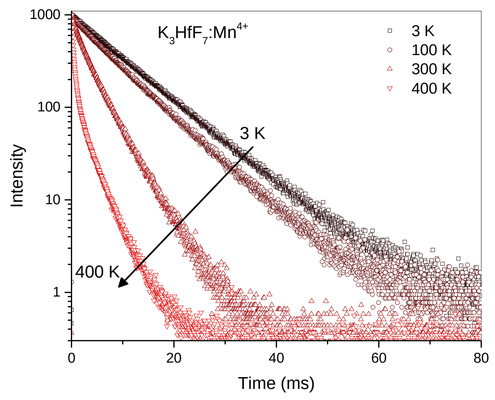


Fig. 8 Lifetime measurements with increasing temperature (Ex = 473 nm; Em = 626 nm) for exemplary chosen temperatures.

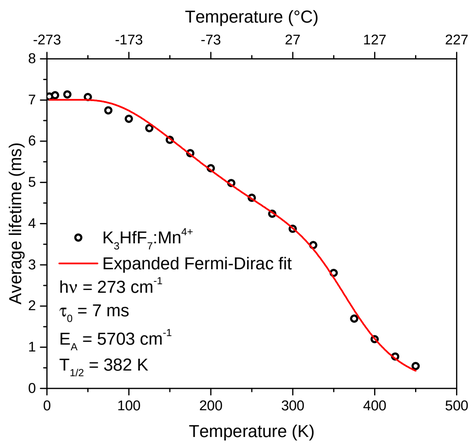


Fig. 11 Average lifetime as function of temperature.

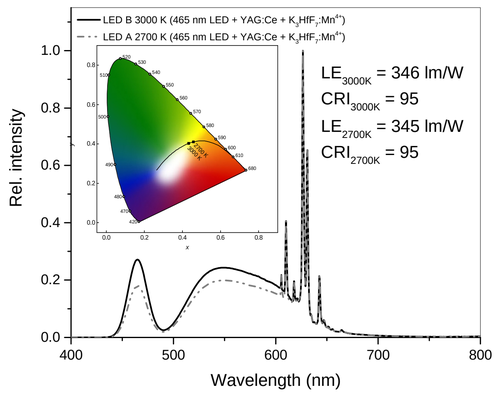


Fig. 12 Emission spectra of warm white LEDs with different correlated color temperatures comprising $K_3HfF_7:Mn^{4+}$ ceramics as a red emitting component. The inset shows the CIE 1931 color space chromaticity diagram with the color coordinates of the two LEDs.

- $K_3Zr_{1-x}Hf_xF_7$ ceramics were successfully synthesized *via* cation-exchange method followed by cold isostatic pressing.
- The band structure of K_3HfF_7 was investigated by DFT calculations and experimentally evaluated with UV reflectance spectroscopy.
- K_3HfF_7 shows a direct band gap at ~6 eV.
- At very low temperature (3 K) distinct Mn^{4+} PL emission from only one highly symmetric octahedral coordinated site can be observed.
- The unusual increase of emission integrals with increasing temperature originates from a progressive increase of the absorption cross section in the low temperature regime.
- The quantum efficiency is close to unity with a Hf content of 20 mol-%.
- The $T_{1/2}$ values can be slightly increased from $K_3ZrF_7:Mn^{4+}$ to $K_3HfF_7:Mn^{4+}$.
- The lifetime recordings show a strong drop of τ due to a progressive mixing with phonons.
- It turned out that $K_3Zr_{1-x}HfxF_7:Mn^{4+}$ ceramics exhibit excellent properties in terms of CRI and LE for use in warm-white pcLEDs.

[1] H. Tan, M. Rong, Y. Zhou, Z. Yang, Z. Wang, Q. Zhang, Q. Wang, Dalt. Trans. 45 (2016) 9654–9660

Acknowledgement

We are grateful for financial support from the Federal Ministry of Education and Research, Germany (ERA.Net RUS Plus, project NANOLED # 361).

CIW FB Chemieingenieurwesen Department of Chemical Engineering

FH MÜNSTER University of Applied Sciences

http://www.fh-muenster.de/juestel