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 ; t@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 to their blue shifted PL in comparison to Mn$^{3+}$ doped oxides. Particularly, $K_2ZrF_6$:Mn$^{3+}$ and $K_2HfF_6$: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 $K_2ZrF_6$:Mn$^{3+}$ and its PL properties have been published. They described the luminescence behavior of Mn$^{3+}$ ions in seven-coordination environment within the $K_2ZrF_6$ 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 $K_2ZrF_6$ and $K_2HfF_6$ 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.

Results and Discussion

Fig. 1: Sketch of the preparation pathway of $K_2(HF_6):Mn^{4+}$ ceramics.


- $K_2Zr_{1-x}Hf_xF_7$:Mn$^{4+}$ ceramics were successfully synthesized via cation-exchange method followed by cold isostatic pressing.
- The band structure of $K_2HfF_6$ was investigated by DFT calculations and experimentally evaluated with UV reflectance spectroscopy.
- $K_2HfF_6$ 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 $T_{2g}$ values can be slightly increased from $K_2ZrF_6$:Mn$^{4+}$ to $K_2HfF_6$:Mn$^{4+}$.
- The lifetime recordings show a strong drop of $\tau$ due to a progressive mixing with phonons.
- It turned out that $K_2Zr_{1-x}Hf_xF_6$:Mn$^{4+}$ ceramics exhibit excellent properties in terms of CRI and LE for use in warm-white pcLEDs.