Photoluminescence of Mn$^{4+}$ activated monoclinic Na$_3$AlF$_6$

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Background

Mn$^{4+}$ activated luminescent materials have attracted much attention recently. Especially alkaline metal hexafluorides, such as K$_3$SiF$_6$:Mn$^{4+}$ or K$_3$TiF$_6$:Mn$^{4+}$, can emit light in the red region under blue or near UV excitation and meet thus the efficiency and color quality of future ‘warm white’ phosphor converted LEDs (pc-LED). However, we investigated the Mn$^{4+}$ photoluminescence (PL) in the well-known monoclinic mineral cryolite (Na$_3$AlF$_6$). We applied a cation-exchange method in order to synthesize Mn$^{4+}$ doped Na$_3$AlF$_6$. Na$_3$AlF$_6$:Mn$^{4+}$ exhibits efficient red photoluminescence peaking at 627 nm, which can be assigned to the $^2$E$_g \rightarrow ^4$A$_{2g}$ intraconfigurational transition of Mn$^{4+}$ ([Ar]3d$^5$ configuration) within the [MnF$_6$]$^{2-}$ octahedra on the aluminium site in the cryolite host structure. Photoluminescence properties, such as temperature dependence of the PL intensity and luminescence lifetime are presented. Colour Rendering Indices (CRI) and Luminous Efficacies (LE) are compared with the well-established phosphor K$_3$SiF$_6$:Mn$^{4+}$.

Synthesis and Structure

![Synthesis of Na$_3$AlF$_6$:Mn$^{4+}$ via one-step (ion diffusion method, and photograph of Na$_3$AlF$_6$:Mn$^{4+}$ under 365 nm UV light excitation and 3K black light](image)

Results and Discussion

![Temperature-dependent emission spectra (left), emission integrals versus temperature with Fermi Dirac fit (middle), lifetime measurements with increasing temperature, inset shows average lifetime T$_{1/2}$ versus temperature (right)](image)

- Na$_3$AlF$_6$:Mn$^{4+}$ was synthesized via a simple and fast one-step method
- Na$_3$AlF$_6$ shows a direct band gap at ~7 eV
- Na$_3$AlF$_6$:Mn$^{4+}$ exhibits bright red photoluminescence peaking at 627 nm. ZPL is at 619 nm with various phonon side bands (stokes and anti-stokes)
- Excitation maxima are at 358 and 466 nm
- Emission shows relatively low quenching behavior with a T$_{1/2}$ value at 392 K
- Internal quantum efficiency is 50% ± 5%
- Lifetime measurements show strong drop of T with increasing temperature. T$_{1/2}$ value at 285 K
- Luminous efficacy and colour rendering values of simulated warm white emitting pcLEDs comprising a dichromatic phosphor blend involving Na$_3$AlF$_6$:Mn$^{4+}$ are calculated and compared to the performance of those warm white emitting pcLEDs comprising K$_3$SiF$_6$:Mn$^{4+}$ (see Fig. 7 and Table 2)

![Time (ms) vs Intensity (Counts)](image)

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