

Photoluminescence of Mn⁴⁺ activated monoclinic Na₃AlF₆

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Background

Mn⁴⁺ activated luminescent materials have attracted much attention recently. Especially alkaline metal hexafluorides, such as K₂SiF₆:Mn⁴⁺ or K₂TiF₆:Mn⁴⁺, 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 Mn⁴⁺ photoluminescence (PL) in the well-known monoclinic mineral cryolite (Na₃AlF₆). We applied a cation-exchange method in order to synthesize Mn⁴⁺ doped Na₃AlF₆. Na₃AlF₆:Mn⁴⁺ exhibits efficient red photoluminescence peaking at 627 nm, which can be assigned to the ²E_g → ⁴A_{2g} intraconfigurational transition of Mn⁴⁺ ([Ar]3d³ configuration) within the [MnF₆]²⁻ octahedra on the aluminum 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 K₂SiF₆:Mn⁴⁺.

Synthesis and Structure

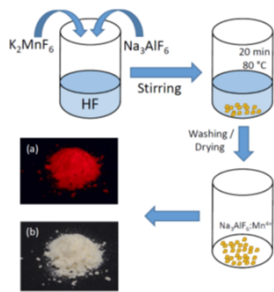


Fig. 1 Synthesis of Na₃AlF₆:Mn⁴⁺ via one step ion diffusion method, and photographs of Na₃AlF₆:Mn⁴⁺ under (a) 365 nm UV light excitation and (b) natural light.

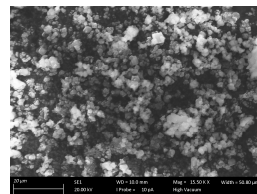


Fig. 2 Typical SEM image of Na₃AlF₆:Mn⁴⁺ (0.1%).

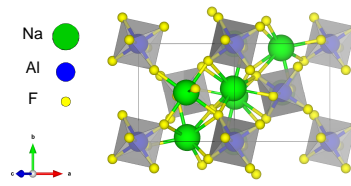


Fig. 3 Crystal structure of monoclinic Na₃AlF₆.

Table 1: Structural data of Na₃AlF₆ (According to Yang et al.)

Na ₃ AlF ₆	
Space group	P12 ₁ /c1 (14)
a / nm	0.54139(7)
b / nm	0.56012(5)
c / nm	0.77769(8)
α, β, γ / °	90, 90.183(3), 90
Al octahedron	
<Al-F1> / pm	227.0
<Al-F2> / pm	223.4
<Al-F3> / pm	229.1
Al site symmetry	1

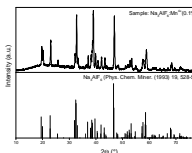


Fig. 4 X-ray (Cu Kα radiation) powder diffraction pattern of monoclinic Na₃AlF₆.

Results and Discussion

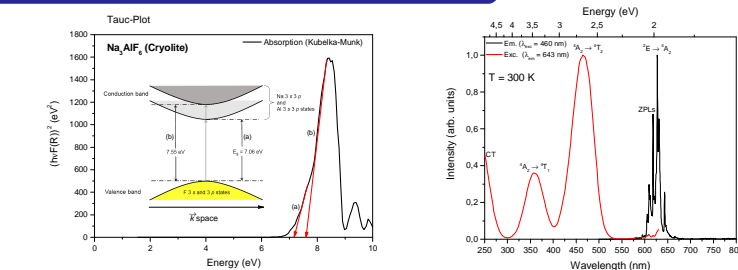


Fig. 5 Tauc plot of undoped Na₃AlF₆ (derived from diffuse UV reflectance measurement), inset shows simplified band structure (left), excitation and emission spectrum of Na₃AlF₆:Mn⁴⁺ (0.1%) at RT (right)

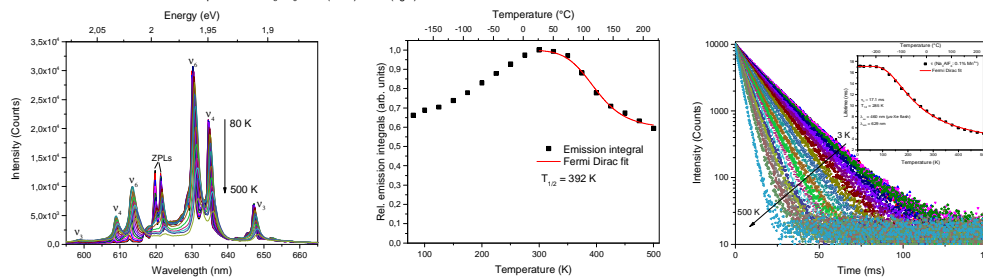


Fig. 6 Temperature-dependent emission spectra (left), emission integrals versus temperature with Fermi Dirac fit (middle), lifetime measurements with increasing temperature, inset shows average lifetime (τ) versus temperature (right).

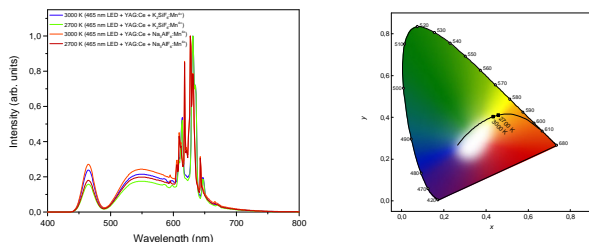


Fig. 7 Simulated emission spectra of warm white emitting pcLEDs comprising a dichromatic phosphor blend involving Na₃AlF₆:Mn⁴⁺ or K₂SiF₆:Mn⁴⁺ (left), calculated color coordinates for 2700 and 3000 K

Table 2: Calculated Racah parameter

⁴ A ₂ → ⁴ T ₂	21501 cm ⁻¹
⁴ A ₂ → ⁴ T ₁	27682 cm ⁻¹
² E → ⁴ A ₂	16103 cm ⁻¹
Dq	2150
B	822
C	3335
β ²	1,050

- Na₃AlF₆:Mn⁴⁺ was synthesized via a simple and fast one-step method
- Na₃AlF₆ shows a direct band gap at ~7 eV
- Na₃AlF₆:Mn⁴⁺ 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 τ 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 Na₃AlF₆:Mn⁴⁺ are calculated and compared to the performance of those warm white emitting pcLEDs comprising K₂SiF₆:Mn⁴⁺ (see Fig. 7 and Table 2)

Table 3: Comparison of CRI and luminous efficacy of 465 nm LED + YAG:Ce + Na₃AlF₆:Mn⁴⁺ or K₂SiF₆:Mn⁴⁺.

CCT	Na ₃ AlF ₆	K ₂ SiF ₆
3000 K	LE = 345 lm/W CRI = 95	LE = 339 lm/W CRI = 95
2700 K	LE = 344 lm/W CRI = 95	LE = 337 lm/W CRI = 93

Acknowledgement

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