Novel Sm^{3+} Molybdates and Tungstates

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Introduction

Since the invention of the blue emitting InGaN LEDs[1], there is a tremendous interest in developing white LEDs for general lighting purposes. The main advantages of the application of LEDs in general lighting are their long lifetime, flexibility, and their high energy efficiency, which might reach 150 lm/W. The first white LEDs were available in 1997, which consist until today of a blue emitting InGaN chip coated by a yellow phosphor (YAG:Ce) to obtain white light by additive colour mixing. This yields cool white LEDs with a high colour temperatures T_c above 4000 K, which do not meet the requirements for ambient lighting.[2]

To obtain warm white LEDs (T_c < 4000 K) the application of an additional red phosphor is required. Presently available warm white LEDs achieves this by the employment of a red band emitter, which is mostly CaS:Eu or $(Ca,Sr,Ba)_2Si_5N_8:Eu^{3+}$, although this goes at the cost of the lumen equivalent. Consequently, the luminous efficiency of a white LED complying YAG:Ce decreases from 50 lm/W to about 30 lm/W, once CaS:Eu is applied as an additional material.
Most important selection criteria for alternative red phosphors in warm-white LEDs are a strong absorption at the emission maximum of the LED die, a high quantum efficiency (>90%), a high stability against O_2, CO_2, H_2O, and under high photon flux.

The goal of this work was the synthesis and optical characterisation of novel Sm^{3+} phosphors for light conversion in LEDs.
The synthesis of molybdates and tungstates, especially the synthesis of Gd_2MO_6, $Gd_2M_2O_9$ and $Gd_2M_3O_{12}$ (M = Mo, W) leads to red emitting phosphor powders with strong and broad f-f-transitions between 400 to 500 nm. Moreover, it is possible to realise a high activator concentration in molybdates and tungstates for Sm^{3+} before concentration quenching due to cross-relaxation sets in. The above mentioned host lattices doped by Sm^{3+} yield luminescent materials with quantum efficiencies of up to 50% for Sm^{3+}. All samples were prepared by a solid state reaction at 1050 °C for 8 h.

Gd_2WO_6

Monoclinic C 1 2/c 1 (#15)

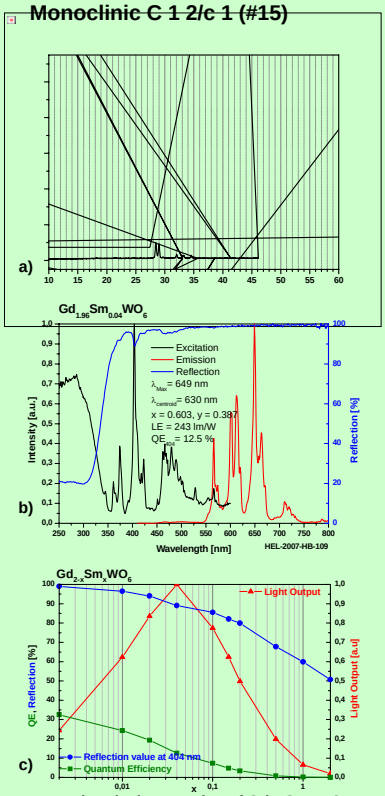

Fig. 1 XRDs and optical properties of $Gd_{2-x}Sm_xWO_6$ samples

a) Powder diffraction patterns b) excitation-, emission- and reflection spectra c) correlation of quantum efficiency, reflection and light output

$Gd_2W_2O_9$

Monoclinic P 1 21/c1 (#14)

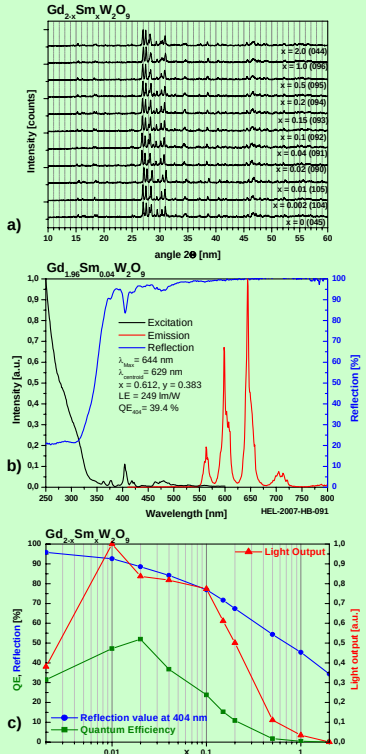

Fig. 2 XRDs and optical properties of $Gd_{2-x}Sm_xW_2O_9$ samples

a) Powder diffraction patterns b) excitation-, emission- and reflection spectra c) correlation of quantum efficiency, reflection and light output

$Gd_2W_3O_{12}$

Monoclinic C 1 2/c 1 (#15)

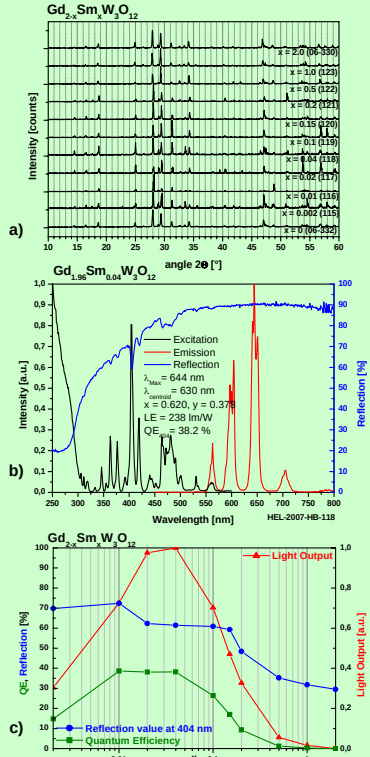

Fig. 3 XRDs and optical properties of $Gd_{2-x}Sm_xW_3O_{12}$ samples

a) Powder diffraction patterns b) excitation-, emission- and reflection spectra c) correlation of quantum efficiency, reflection and light output

Conclusions

Fig. 1a to 3a show the powder diffraction patterns of prepared samples, which proof isomorphism for the substitution from Gd^{3+} to Sm^{3+}. All samples of Ln_2WO_6, $Ln_2W_2O_{12}$ and $Ln_2W_3O_{12}$ (Ln = Gd, Sm) are of single phase.

For all excitation, emission and reflection spectra (Fig. 1b to 3b) strong 4f-4f transitions in the reflection and excitation spectra can be observed at 404 nm. The emission spectra showing the typical red Sm^{3+} emission with its main transitions lines at 560 nm ($^4G_{5/2}$-$^6H_{5/2}$), 600 nm ($^4G_{5/2}$-$^6H_{7/2}$), 650 nm ($^4G_{5/2}$-$^6H_{11/2}$) and 700 nm ($^4G_{5/2}$-$^6H_{11/2}$)

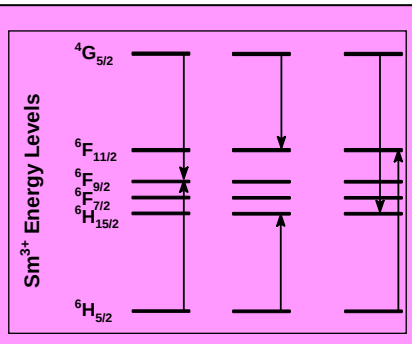

Fig. 4 Simplified sketch of Sm^{3+} energy levels with possible pairs of cross-relaxation transitions[4]

Unusual high concentrations of Sm^{3+} can be realised with quantum yields up to 35% for Gd_2WO_6 with 0.1 mol% Sm^{3+}, 52% for $Gd_2W_2O_9$ with 1% Sm^{3+} and 40% for $Gd_2W_3O_{12}$ with 0.05% to 0.2% Sm^{3+} (Fig. 1-3c).

Due to cross-relaxation processes (Fig. 4) Sm^{3+} luminescence is mostly quenched at a rather low dopant concentration. In tungstates and molybdates the Sm^{3+} concentration can be rather high before cross-relaxation sets in due to the distinct separation of Sm^{3+} ions from each other by the bulky molybdate and tungstate groups.

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References
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