Nanoscale Y_2O_3:Eu^{3+} and (Y,Gd)VO_4:Eu^{3+}(Bi^{3+}) Powders for Application in Micro Optical Structures

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Background

To achieve high color rendering white light sources based on InGaN LEDs it is necessary to add additional red emission to the conventional cool white YAG:Ce coated LEDs. This is feasible by the application of an additional red line emitting phosphor. Efficient line emitting red phosphors are e.g. Y_2O_3:Eu, (Y,Gd)VO_4:Eu, Y_2O_2S:Eu and $Y_3Al_5O_{12}$:Eu. Main problem of this approach is the weak absorption due to the 4f-4f transitions located in the blue spectral range. By incorporation of the Eu^{3+} doped luminescent materials into a photonic crystal, such as inverse opals, the weak absorption in the blue spectral range should be enhanced.

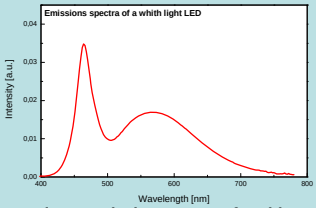

Fig. 1: Emission spectra of a white light LED comprising YAG:Ce

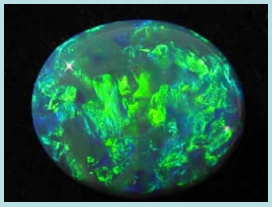

Fig. 2: Natural opal

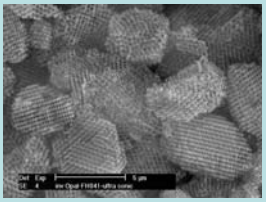

Fig. 3: Morphology of an as synthesized inverse SiO_2 opal

Synthesis of Y(Gd)VO_4:Eu^{3+}(Bi^{3+}) (Fig. 4)

First samples were prepared in ethylenglycol (EG) under hydrothermal conditions in a pressure reaction vessel described by Nanosolutions GmbH [1]. This led to nanoparticles with an average size of 60 to 80 nm, which are dispersible in water (Fig. 5).

Moreover, it was attempted to precipitate $GdVO_4$:Eu^{3+} from aqueous solution, which yield in particles with low crystallinity and an average size of 60 nm. Sintering of the particles increased the efficiency and crystallinity (Fig. 6).

Surface complexation of the nanoparticles by acetylacetonate ligands yields efficient sensitization in the range from 340 to 420 nm (Fig. 7).

First precipitation trials within the cavities of an inverse SiO_2 opal were not yet successful due to the required high pH-value (12 to 13) produced from the orthovanadate, which destroyed the substrate.

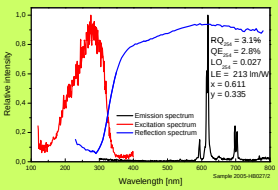

Fig. 4 : YVO_4:Eu^{3+} (5 %)

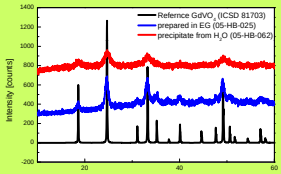

Fig. 5: X-ray diffraction powder pattern

Fig. 6: Image of heat treated $GdVO_4$:Eu^{3+}; 2h at RT, 200 °C, 300°C, 400 °C, 500 °C and 600 °C

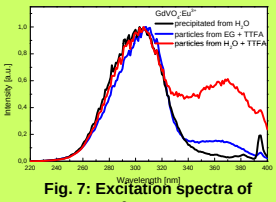

Fig. 7: Excitation spectra of $GdVO_4$:Eu^{3+} (5 %) with and without surface complexation

Synthesis of Y_2O_3:Eu^{3+}

Y_2O_3:Eu^{3+} was prepared by pyrolysis of $Y(C_2O_4)_3$-precursors as described by Chen et. al. [2]. From temperature dependent x-ray diffraction experiments it can be concluded that the precursor material was completely transformed at 550°C to the cubic Y_2O_3 phase (Fig. 8).

The average particle size could be reduced by the application of ethanol and 1-methoxy-2-propanol during the precipitation process from 70 - 80 nm down to 20 - 30 nm (Fig. 9).

However, these particles are still to large to penetrate the pores of the inverse opal, that first loading experiments were not yet successful.

As an alternative to infiltration by nanoparticles, next investigations will concentrate on the pyrolysis of precursors like Yttrium oxalate, Yttrium hydroxide, Yttrium-EDTA-, Yttrium-citrate- and Yttrium-tartrate-complexes, which can be transformed into the oxide below 600°C.

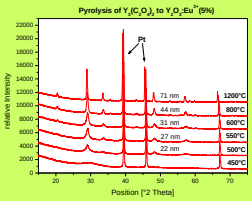

Fig. 8 Temperature dependent XRDs

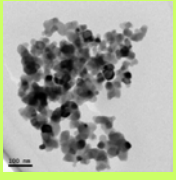

Fig. 9 TEM image of Y_2O_3

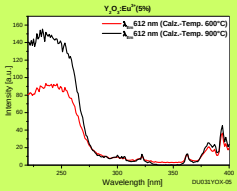

Fig. 10 Excitation spectra of nanoscale Y_2O_3:Eu^{3+} (600° and 900°C)

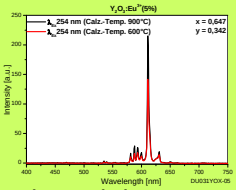

Fig. 11 Emission spectra of nanoscale Y_2O_3:Eu^{3+}(600° and 900°C)

[1] T. Heidelberg, C. Meyer, I. Kühl, *Synthesis of nanoparticles comprising metal (III)vanadate*. 2004, Nanosolutions, WO 002004096714

[2] T.-M. Chen, S.C. Chen, C.-J. Yu, *J. Solid State Chem.*; 1999, *144*, 437-441