

Colour on Demand YAG:Ce for Application in White pcLEDs

Introduction

To achieve white light by a blue emitting InGaN die a yellow emitting luminescent screen is deposited onto the chip that converts an appropriate part of the blue radiation emitted by the chip into yellow to orange light. This results due to additive colour mixing in a white light source with a colour temperature between about 3000 and 10000 K, depending on the optical thickness of the phosphor layer and on the spectral position of the phosphor's emission band. The most widely applied phosphor in white LEDs is cerium doped yttrium aluminium garnet (YAG:Ce) that shows strong absorption in the blue and a broad emission band, whereby its emission peak position can be widely tuned by the composition of the host lattice.

The energetic position of the underlying [Xe]5d¹ to [Xe]4f¹ transition of trivalent cerium is a sensitive function of the crystal-field strength at the dopant site and the covalent character of the host lattice. Co-doping of YAG:Ce by trivalent rare earth ions such as lutetium, for example, leads to a green shift of the emission band whereas co-doping by gadolinium or terbium leads to a red shift of the emission band due to the increasing covalency. We found that attempts to increase the red shift by co-doping with both ions at the same time, just results in the opposite. The emission band of YAG:Ce,Tb,Gd is shifted to the green with an increasing gadolinium content and decreasing terbium content. Based on these findings, we will show that a wide range of YAG:Ce phosphors with a colour point on demand of the given application can be made.

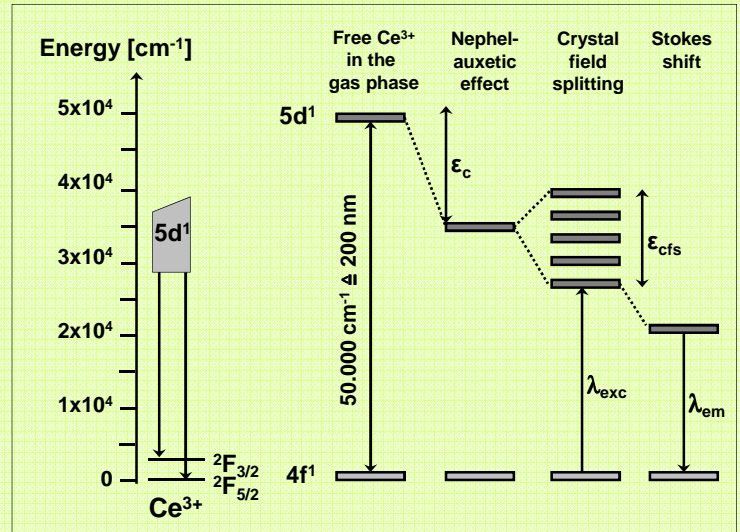


Fig. 1: Simplified term scheme of the trivalent Cerium ion: influence of the chemical surrounding on the excitation and emission energy [1]

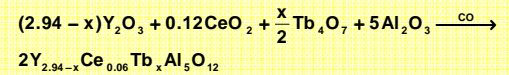
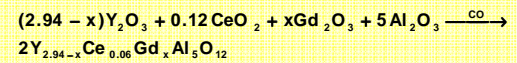
Element	Ionic charge	Coordination number	Ionic radius (pm)
Yttrium	3+	8	115
Dysprosium	3+	8	116,7
Terbium	3+	8	118
Gadolinium	3+	8	119,3
Samarium	3+	8	121,9
Neodym	3+	8	124,9
Praseodym	3+	8	126,6
Cer	3+	8	128,3

Tab. 1: Possible Co-Dopants [2]

Synthesis

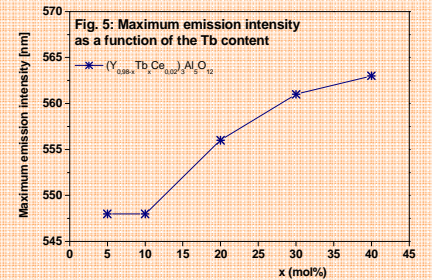
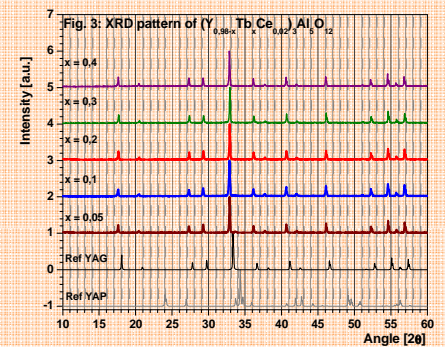
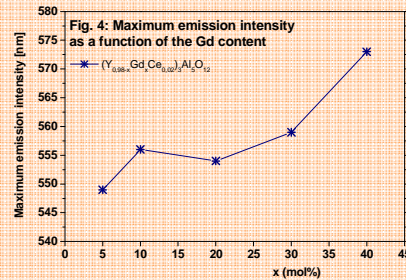
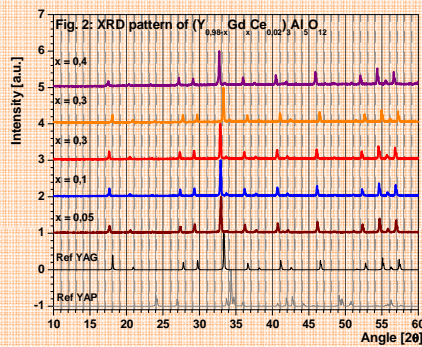
Samples were prepared by a mixing and firing route [3]: The oxides Y₂O₃, Al₂O₃, CeO₂ and Gd₂O₃ resp. Tb₄O₇ were blended in the appropriate stoichiometric amount and thoroughly milled. The calcination was done in two steps, both in a reducing atmosphere of CO: In the first step the precursor was heated for 2 h at 1200 °C, after regrinding the intermediate product the final calcination was done at 1650 °C for 6 h.

Solid state reaction:



Results and Conclusions

The experiments have shown that the substitution of Y³⁺ in YAG:Ce by larger cations shifts the emission band to longer wavelengths. The reasons for that can be found in the influences of such a substitution on the host lattice: Because of the size of the co-dopant there is a distortion in the lattice and the lattice constant of the cubic garnet lattice increases. This results in a higher covalency and the energy difference between the excited and the ground state gets smaller. That there is a change in the crystal lattice can be seen in the XRD pattern as show in Fig. 2 and Fig. 3. The samples co-doped with Gd³⁺ are not phase pure, there is a small amount of a (Gd,Ce)AlO₃. If Tb³⁺ is used as co-dopant the samples show a phase pure XRD pattern. In Fig. 4 and Fig. 5 the wavelengths with the maximum emission intensity are plotted as a function of the co-dopant content. There can be seen a red shift for an increasing content of either Gd³⁺ or Tb³⁺.



References

- Jüstel, T.: Lecture 'Incoherent Light Sources', Summer term 2007
- Hulsey, J.E.: Inorganic Chemistry, 3rd edition, Harper International SI Edition, Cambridge 1983.
- Wu, J., L. Denbars, S. P. Srdanov, V. Weinberg, H., Cerium Doped Garnet Phosphors for Application in White GaN-based LEDs, Mat. Res. Soc. Symp. Proc. Vol. 667, G5.1.1-G51.6 (2001)