On the VUV Luminescence and Degradation of UV-C Emitting Phosphors

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1. Phosphor converted Xe DBD lamps

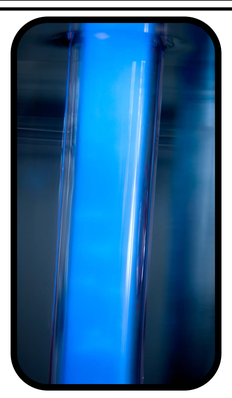


Fig. 1 Xe-DBD Lamp operated in water.

Dielectric barrier Xenon excimer discharge lamps are known as efficient sources of vacuum ultraviolet radiation, while the main band peaks at 172 nm.[1] By the use of VUV excitable conversion materials which are applied as a coating layer onto the lamp body it is feasible to manufacture efficient UV-C, near VUV, or even UV-A/B emitting Xe excimer lamps which may perform well for the replacement of established Hg discharge lamps and respective UV radiation systems.

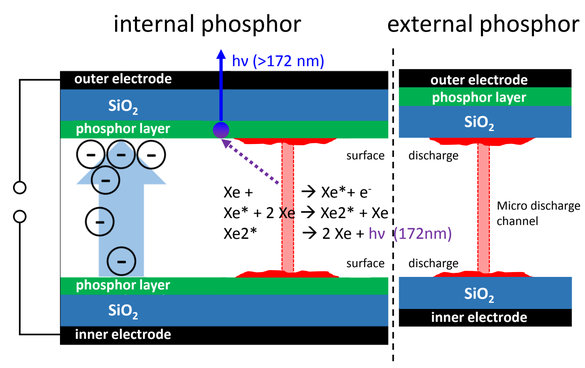


Fig. 2 Schematic illustration of the principle of operation of two different phosphor converted Xe-excimer DBD lamp patterns.

2. UV emitting LnPO4:X phosphors for Xe DBD lamps – effective disinfection

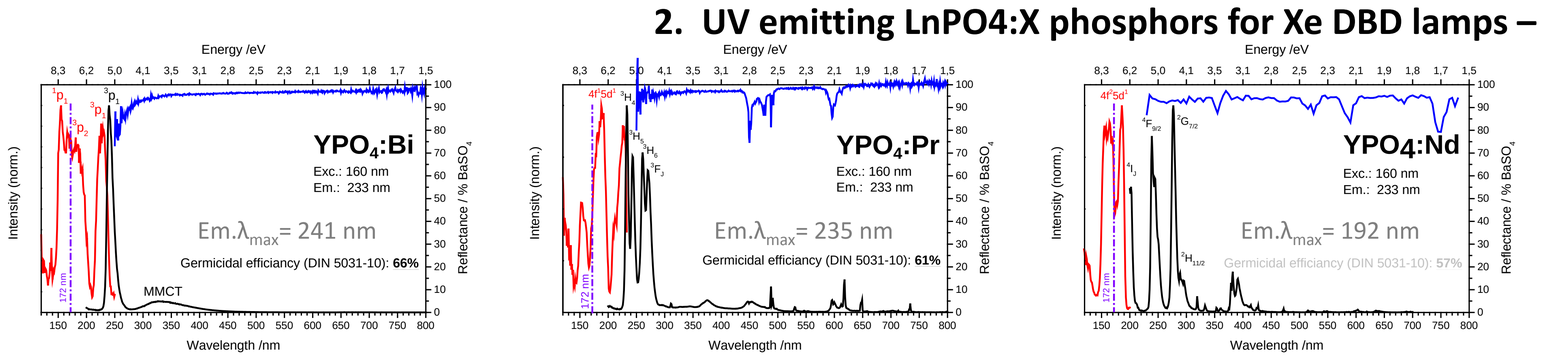


Fig. 3 VUV-excitation-, emission and reflectance spectra of the UV-C emitting phosphors YPO_4:Bi and YPO_4:Pr and the VUV-Emitting Phosphor YPO_4:Nd, respectively

YPO_4 is a radiation stable wide band gap material (Δ_{BG} = 9.2 eV) which turns into a very efficient UVC / VUV emitter upon doping with e.g. Pr^{3+}, Bi^{3+}, or Nd^{3+}.[2],[3] Doping with Bi^{3+} leads to an emission band peaking at 241 nm due to a s-p transition of the $[Xe]4f^{14}5d^{10}6s^2$ cation, whereas a doping with Pr^{3+} or Nd^{3+} leads to a maximum emission around 235 and 192 nm, respectively. This emission is due to f-d transitions of the trivalent lanthanides.

YPO_4:Bi^{3+}/Pr^{3+}/Nd^{3+} comprising lamps can be used as efficient UV-C or VUV light sources in disinfection

The germicidal efficacy typifies a useful tool to evaluate a phosphor for its disinfection suitability

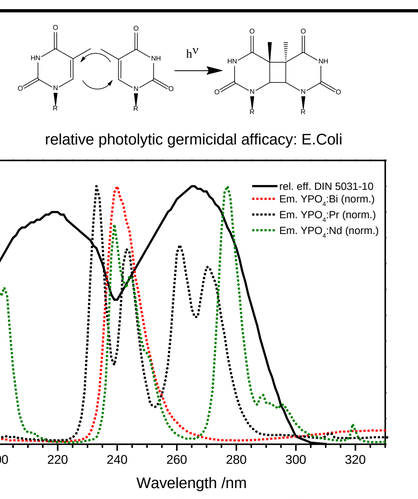


Fig. 4 relative photolytic disinfection efficacy for Escheria Coli according DIN 5031-10

3. Device lifetime limitations: aging effects on $LnPO_4$ based phosphor materials within an Xe excimer discharge

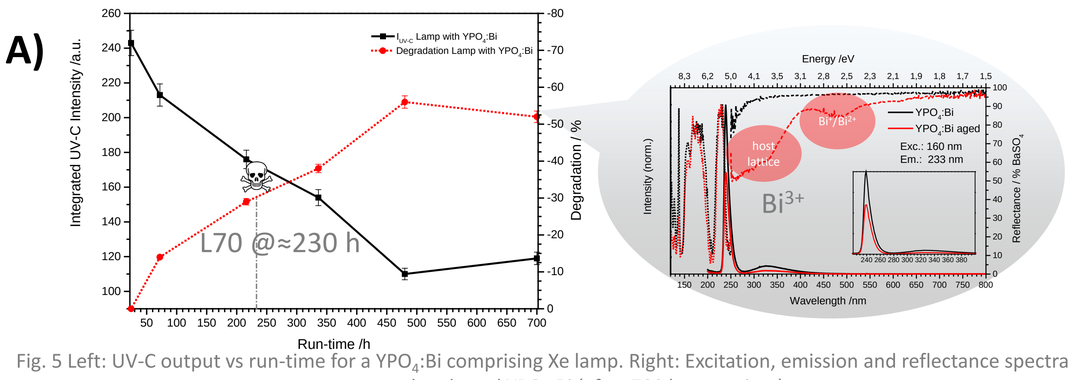


Fig. 5 Left: UV-C output vs run-time for a YPO_4:Bi comprising Xe lamp. Right: Excitation, emission and reflectance spectra of untreated and aged YPO_4:Bi (after 700 hrs run-time)

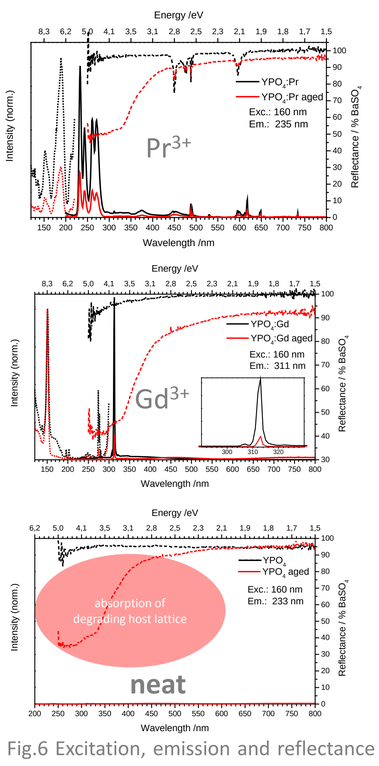


Fig.6 Excitation, emission and reflectance spectra of aged and untreated YPO_4:Pr, YPO_4:Pr, YPO_4

Phosphor converted Xe excimer lamps comprising YPO_4:Bi (internal phosphor) exhibit a distinct and fast characteristic aging under continuous operation:

- Observable greying of the actually clear white phosphor coating
- Continuous decrease of UV radiation output over operation time (after 24 h forerun)
- A dimming of 30 % (L70) is already reached after ≈ 230 hours run-time

Spectroscopy of aged YPO_4 and YPO_4 doped with Bi^{3+}, Pr^{3+} and Gd^{3+}, respectively reveals:

- The distinct aging effect is evident regardless the dopant cation and is as well observed for the undoped host material YPO_4
- As a detectable main symptom of aging, a novel broad emission band appears rising from the visual beginning at around 500 - 600 nm towards the UV region
- The uprising absorption band may be accompanied by a general overall absorption (greying) and a absorption band ascribed to a reduced activator species in case of YPO_4:Bi (Bi^{3+} → Bi^{+}/Bi^{2+})
- **Upon PL excitation into the new host absorption bands in the UV yields deep red luminescence, regardless which or any doping. This phenomenon was further followed by the temperature dependent PL spectra of aged undoped YPO_4, $LaPO_4$, and $LuPO_4$ (see B)**

B)

Optical grade YPO_4, $LuPO_4$ and $LaPO_4$ were aged analogous to the doped phosphor materials. All analysed ortho-phosphates exhibit comparable aging effects indicated by characteristic photoluminescence

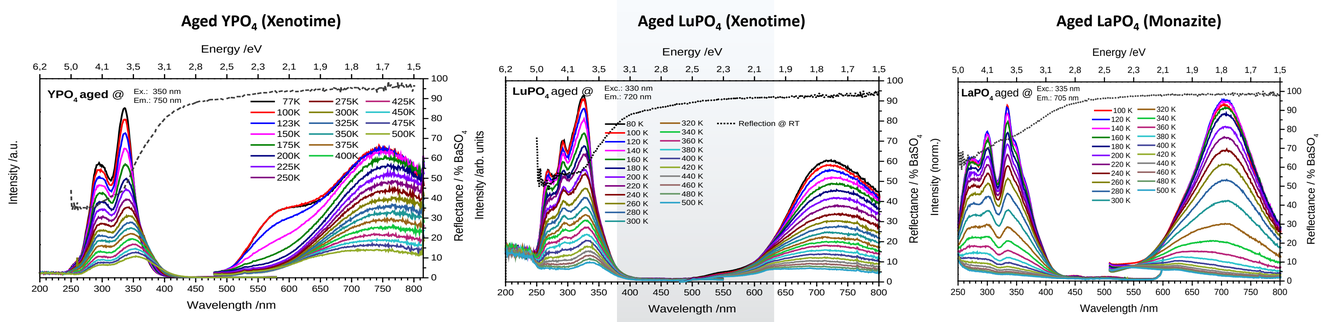


Fig. 7 Temp. dependent excitation and emission spectra measured from aged samples of YPO_4, $LuPO_4$ and $LaPO_4$.

YPO_4 & $LuPO_4$ structure (Xenotim, $I4_1/amd$)

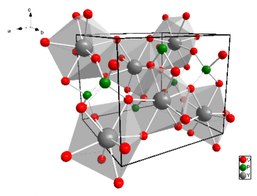


Fig. 9 Xenotime structure

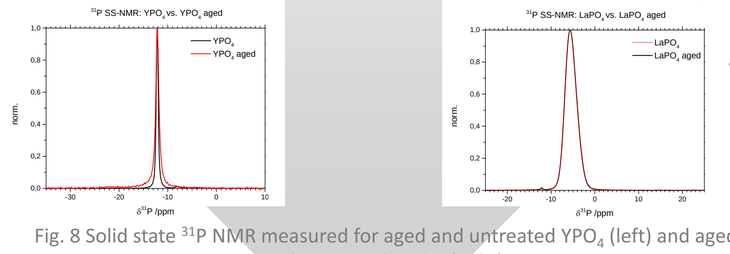


Fig. 8 Solid state ^{31}P NMR measured for aged and untreated YPO_4 (left) and aged and untreated $LaPO_4$ (right).

$LaPO_4$ structure (Monazit, $P2_1/c$)

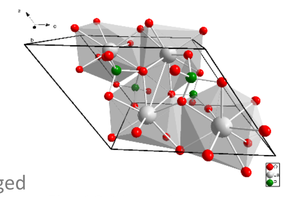
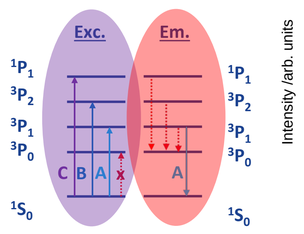
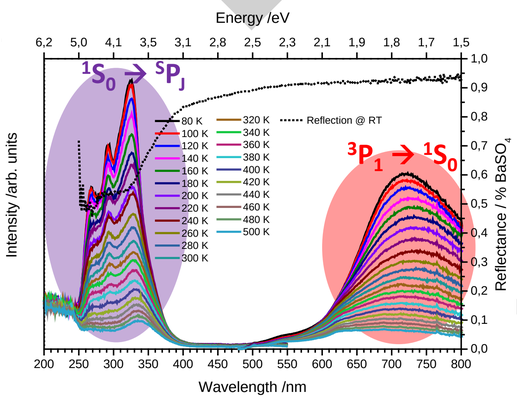


Fig. 10 Monazite structure

Solid State NMR reveals that the bulk host material remains unaltered (within the detection limits)

Energy level scheme for nS^2 luminescence





The apparent photo-luminescence shows features characteristic for ns^2 cations e.g. Bi^{3+}, Sb^{3+}, As^{3+}

P^{+V} [Ne]$3s^0$ → P^{+III} [Ne]$3s^2$

Reduction of P^{5+} by hot e^- and $Xe^{+\cdot}$ impingement in plasma contact

Fig. 11 Left: Energy level scheme for ns^2 luminescence; Middle: Temp. dependent excitation and emission spectra measured from aged samples of $LuPO_4$ supplemented by proposed electron transitions; Right: Proposed scheme for P^{5+} reduction due to plasma contact

4. Device lifetime improvement: Application and impact of protective inert particle coatings

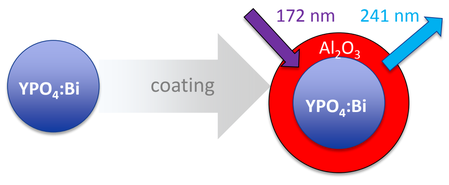


Fig. 13 Illustration of YPO_4:Bi a particle coated with a protective but 172 nm transmitting Al_2O_3 layer or shell.

Particle Coating:
Ideally, each and every single phosphor particle is coated with an homogeneous and surface covering coating of α-Al_2O_3 to prevent phosphor aging (degradation) under exposure to the Xe discharge.

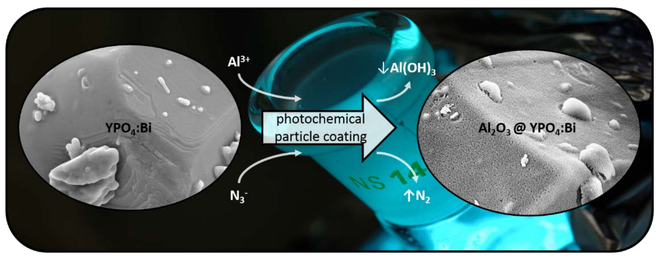


Fig. 13 Illustration of UV driven particle coating process [4]

An optimal coating quality in terms of homogeneity and particle surface coverage were yielded with a photochemically driven precipitation process, recently described in literature. [4]

For further information look up literature 4 or follow

The application of an Al_2O_3 coating onto YPO_4:Bi particles results in a reduced phosphor degradation (approximately factor ≈ 2) with respect to an uncoated material and under analogous aging conditions

This positive effect appears to act upon the reduction of the activator Bi^{3+} as well as the degradation of the host material itself, as indicated by the comparison of spectra displayed by figure 14.

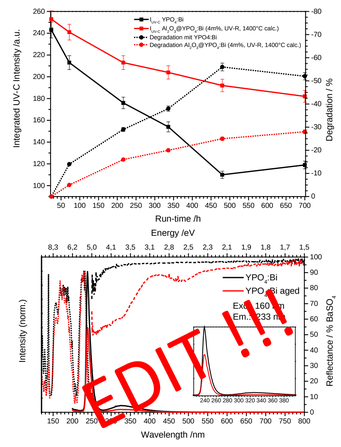


Fig. 14 Fig. Top: UV-C output vs run-time for a YPO_4:Bi and a Al_2O_3 coated YPO_4:Bi comprising Xe lamp. Bottom: Excitation, emission and reflectance spectra of the aged YPO_4:Bi and Al_2O_3 coated YPO_4:Bi (after 700 hrs run-time)

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Literature

[1] U. Kogelschatz,, Plasma Chem. Plasma Process **23** (2003) 1
[2] P. Dorenbos for band gap 9,25 eV
[3] T. Jüstel, P. Huppertz, W. Mayr, D.U. Wiechert, J. Luminescence **106** (2004) 225
[4] M. Broxtermann, T. Jüstel, Mater. Res. Bull. **80** (2016) 249