On the Temperature and Time Dependent Photoluminescence of $Lu_3Al_5O_{12}:Gd^{3+}$

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Background

- Presently, UV-B emitting LEDs with a sufficiently high operational lifetime and wall plug efficiency are not available
- Use of mercury-vapor discharge lamps for UV applications
  - low lifetimes and limited efficiency
- Phosphor coated Xe excimer lamps for:
  - medical treatment (Vitiligo, Psoriasis)
  - life science (tanning)
  - chemistry (photochemistry)
  - UV-curing (polymer hardening)

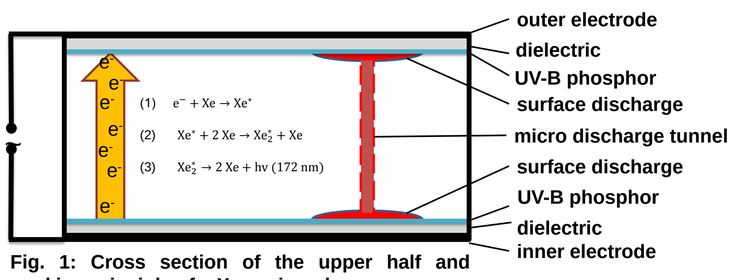

Fig. 1: Cross section of the upper half and working principle of a Xe excimer lamp.

Experimental Section

Combustion synthesis

- $Al(NO_3)_3 \cdot 9H_2O$ was dissolved in H_2O
- Metal oxides - Gd_2O_3, Lu_2O_3 - were dissolved in boiling HNO_3
- The solutions were quantitatively added up
- Tris(hydroxymethyl)aminomethan (TRIS) was added in a molar ratio of 2:1 (TRIS:cations)
- Water was evaporated at 80 °C and a transparent gel was formed
- The gel was burned at 300 °C in a self-propagating reaction and dried at 150 °C for several hours
- The black powder was pre-fired at 900 °C for 6 h to remove organic residuals
- The received white powder was crushed and annealed at 1600 °C for 8 h

Structure

- $Lu_3Al_5O_{12}$ belongs to the garnet family and has a cubic crystal system
- General structure of garnets is $^{[8]}X_3{}^{[6]}Y_2[^{[4]}ZO_4]_3$
- Lu^{3+} cations occupy the X-sites
- Al^{3+} cations occupy the Y- and Z-sites
- Lu^{3+} was substituted by Gd^{3+}
- Space group: $Ia\bar{3}d$ (#230)

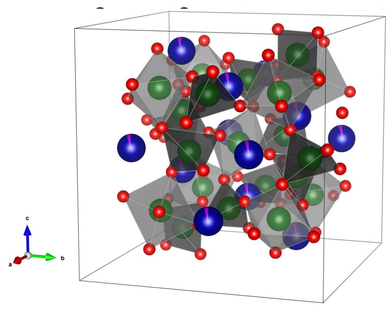

Fig. 2: Unit cell of $Lu_3Al_5O_{12}:Gd^{3+}$. Red balls → O^{2-}, Blue balls → Lu^{3+}/Gd^{3+}, Green balls → Al^{3+}.

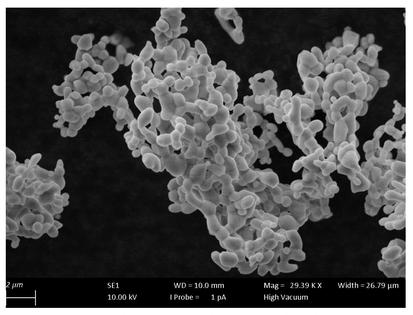

Fig. 3: SEM image of $(Lu_{2.85}Gd_{0.15})Al_5O_{12}$.

Results and Discussion

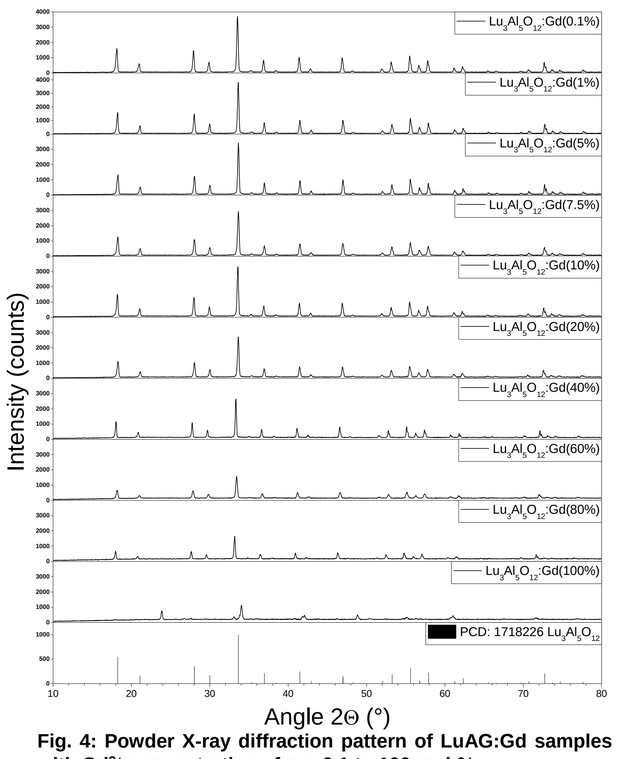

Fig. 4: Powder X-ray diffraction pattern of LuAG:Gd samples with Gd^{3+} concentrations from 0.1 to 100 mol-%.

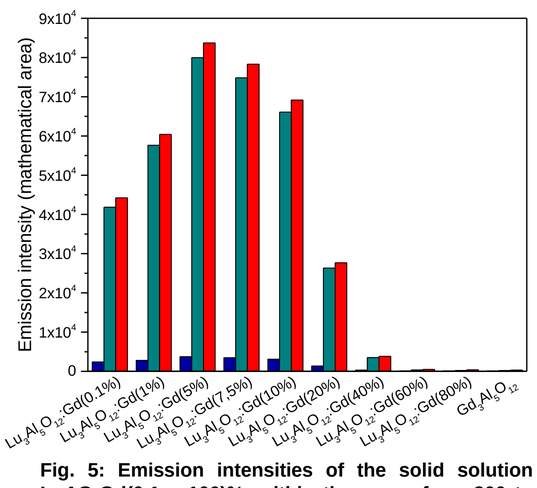

Fig. 5: Emission intensities of the solid solution LuAG:Gd(0.1 – 100)%, within the range from 300 to 310 nm (blue), 310 to 320 nm (cyan) and 300 to 320 nm (red).

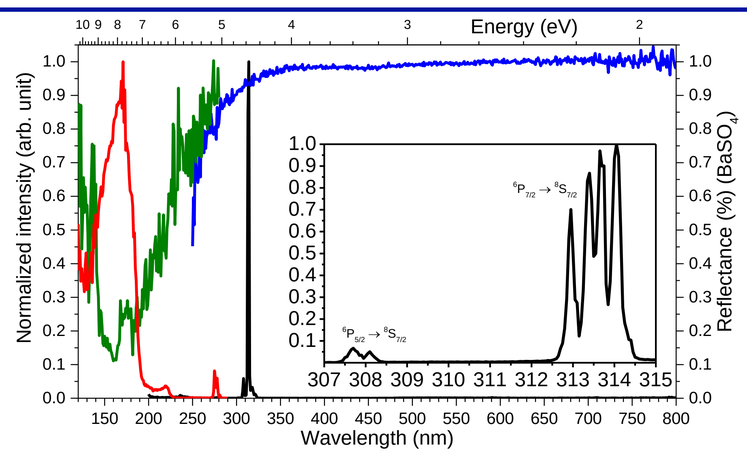

Fig. 6: VUV-reflection- (green), reflection- (blue), excitation- (red) and emission-spectra (black) of LuAG:Gd^{3+}(5%). The inset shows an enlarged emission spectra in the range from 307 to 315 nm.

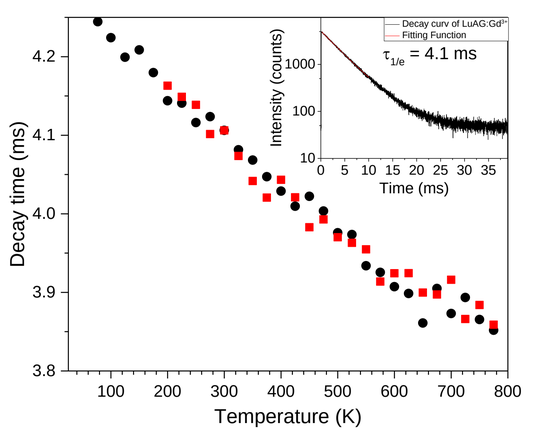

Fig. 7: Temperature dependent decay times of the main transition $^6P_{7/2} \rightarrow {}^8S_{7/2}$ (black) and $^6P_{5/2} \rightarrow {}^8S_{7/2}$ (red) transitions. The inset shows the decay curve of the main emission band measured at RT.

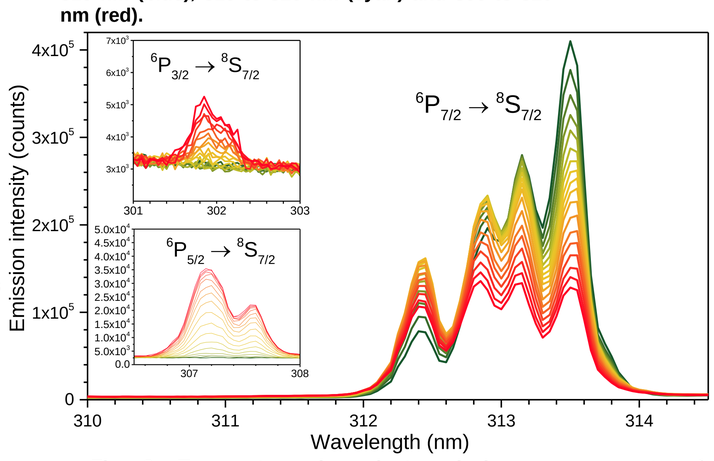

Fig. 9: Temperature dependent emission measurements of LuAG:Gd^{3+}(5%) from 77 to 500 K within the range from 310 to 314.5 nm. The upper and lower inset shows the emission of the $^6P_{3/2} \rightarrow {}^8S_{7/2}$ and $^6P_{5/2} \rightarrow {}^8S_{7/2}$ transition of Gd^{3+}, respectively.

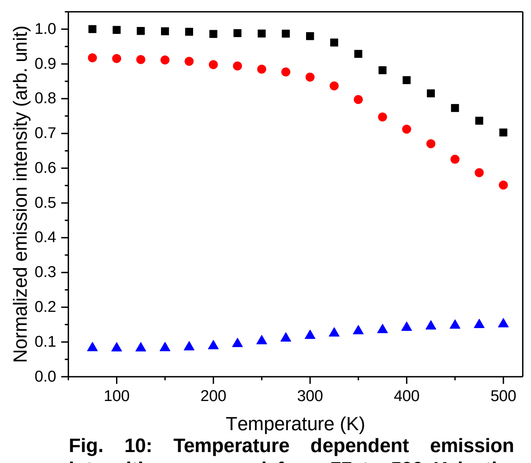

Fig. 10: Temperature dependent emission intensities measured from 77 to 500 K in the range from 300 to 310 nm (blue), 310 to 320 nm (red) and 300 to 320 nm (black).

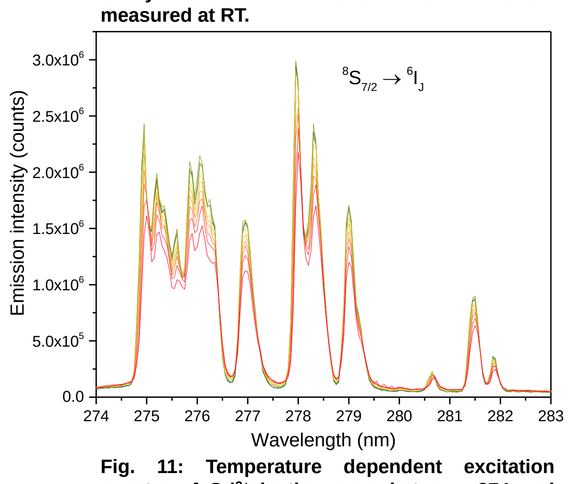

Fig. 11: Temperature dependent excitation spectra of Gd^{3+} in the range between 274 and 283 nm. The excitation band is assigned to the $^8S_{7/2} \rightarrow {}^6I_J$ transition.

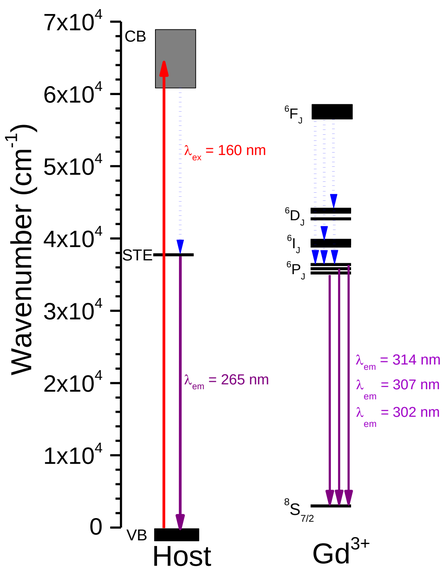

Fig. 8: Energy level diagram of LuAG and Gd^{3+}, which shows the excitation of the host lattice and emission of the Gd^{3+} ion.

- LuAG has a band gap of 7.2 eV and thus a white body color. According to its band gap the excitation maximum peaks at 172 nm, which is where the Xe emission culminate.
- LuAG:Gd^{3+} shows intense line emission peaking at 313.7 nm, which splits into four sublines due to the crystal field splitting. The emission is attributed to the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition.
- A second and third emission band peaks at 302 and 307.5 nm. They belong to the $^6P_{3/2} \rightarrow {}^8S_{7/2}$ and $^6P_{5/2} \rightarrow {}^8S_{7/2}$ transitions, respectively.
- The emission intensity of the main emission band at 313.7 nm decreases with increasing temperature while the emission band at 307.5 and 302 nm rise with increasing temperature.
- As usual, emission intensity decreases from 77 to 500 K (thermal quenching).
- The excitation spectra show a continuous decrease in intensity with increasing temperature and no shift of the excitation band.
- The decay times decrease in a linear way when the temperature is increased from 77 to 500 K. This holds true for the $^6P_{5/2} \rightarrow {}^8S_{7/2}$ as well as the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition.

Conclusions

- A series of LuAG:Gd^{3+} samples of single phase with a Gd concentration between 0.1 and 80 mol-% was obtained.
- LuAG:Gd^{3+} with 5 mol-% Gd^{3+} shows the highest emission intensity.
- LuAG:Gd^{3+} is an intense UV-B emitting material under VUV (λ_{ex} = 160 nm) excitation, which shows three emission lines peaking at 313.7, 307.5, and 302 nm.
- Xe excimer lamps comprising LuAG:Gd can be regarded as an alternative to mercury low-pressure lamps or UV-B emitting LEDs.
- LuAG:Gd might also be a material for temperature sensing applications due to the change of the line ratio.

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