Photochemically produced nanocrystalline garnet materials

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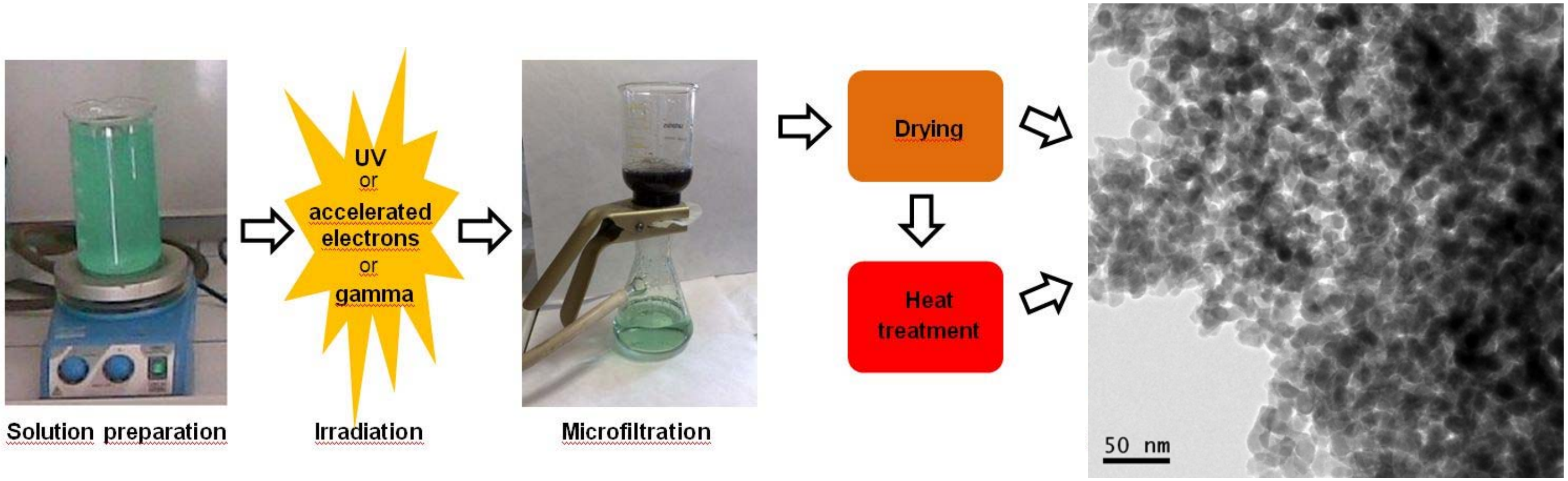
Introduction

- Radiation-induced preparation of garnet materials:
  - RE^{3+}, Al^{3+}, … in aqueous solution of ammonium formate
  - Irradiation by UV light / ionizing radiation yields precipitate
  - Mild thermal treatment (down to 850°C) – garnet crystallization; high luminescence intensity at higher temp.
  - Nanocrystalline (size increases with calcination temperature)
  - Pilot plant: ~ 70 g of LuAG per batch

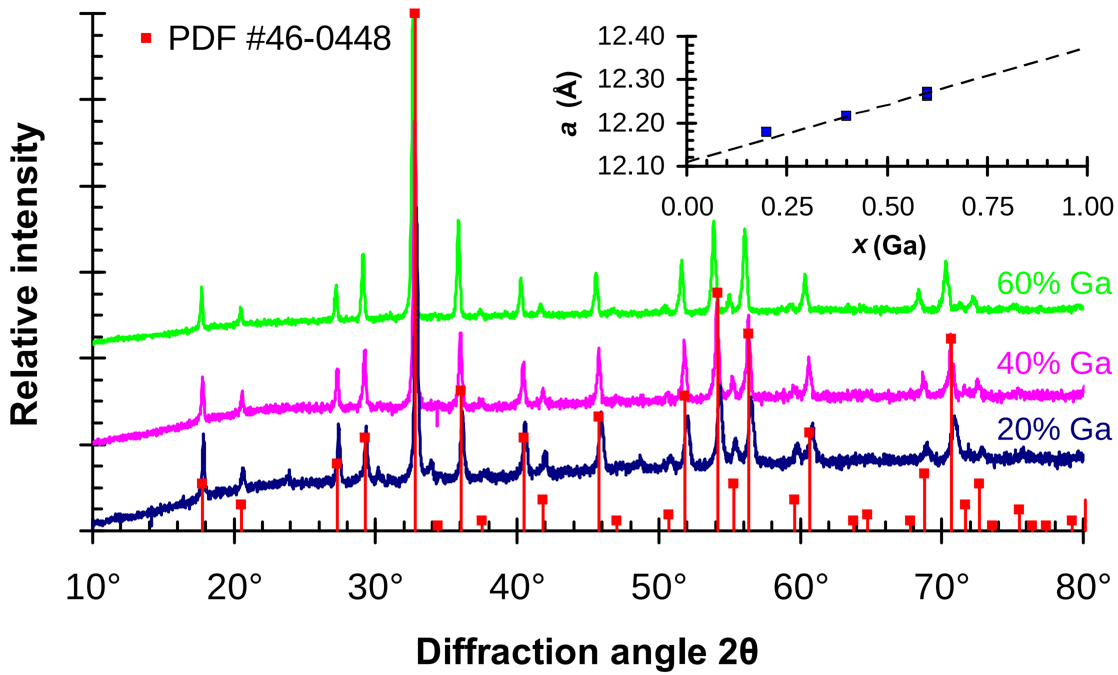


- Many metal ions can be used. Goal: more complicated garnets ☺

GGAG – preparation

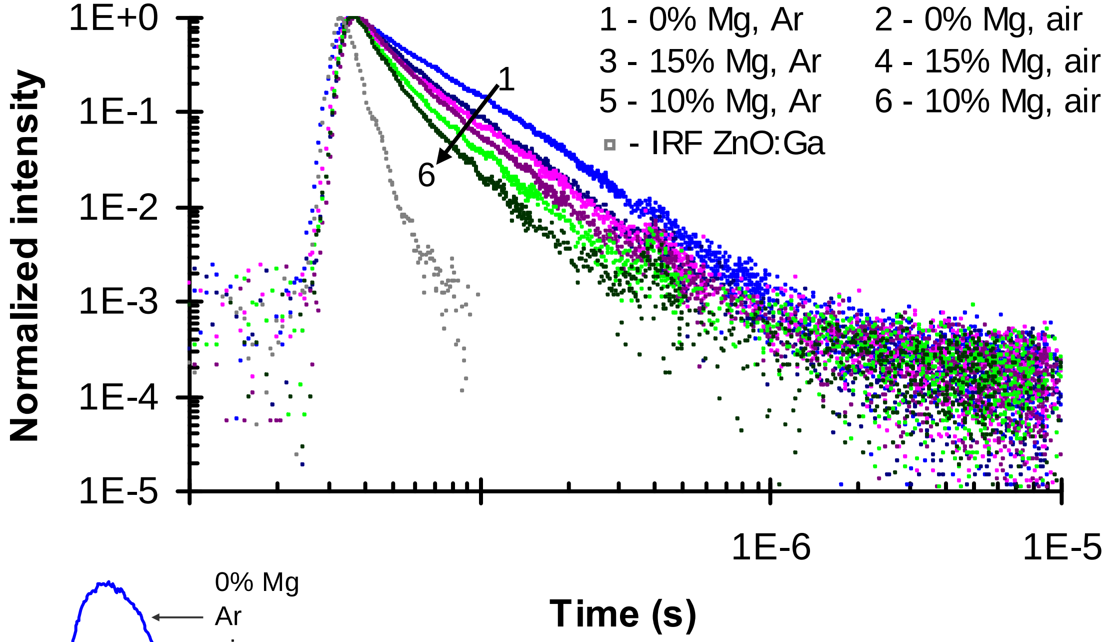
- Very efficient garnet scintillator (Ce-doped); Ga lowers the conduction band: elimination of Gd_{Al} defects
  - $Gd_3(Ga_xAl_{1-x})_5O_{12}$, unstable GAG (x=0) with respect to $GdAlO_3$; at high x, Ce^{3+} excited state lies in conduction band
  - GaO_x can evaporate during heating (solution: add O_2)
  - Vegard's law – lattice parameter *a* rises linearly with x

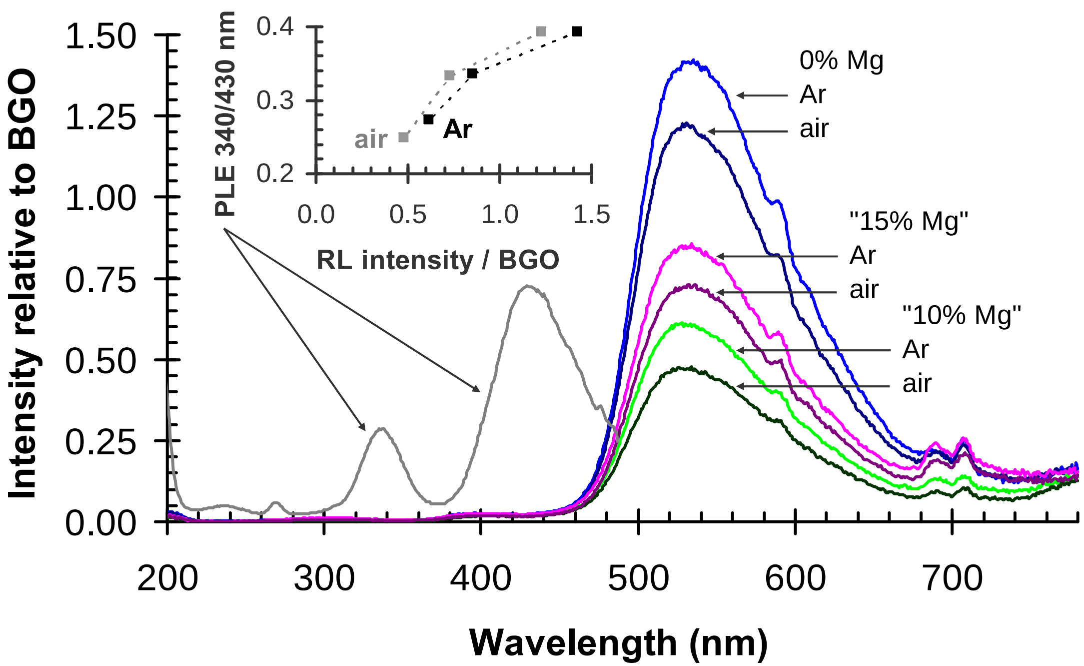
- Relative to YAG or LuAG, higher temperatures (1400–1500 °C) are needed
- Impurities: $Gd_2(GaO_4)O_2$ $GdAlO_3$ $Gd_4Al_2O_9$



GGAG – Ce^{4+}: air / Mg

- Defect engineering = Mg^{2+} addition to stabilize Ce^{4+} ions (shortening of the decay time)
- Calcination in air causes the same





☹ Mg doping through radiation method is unreliable

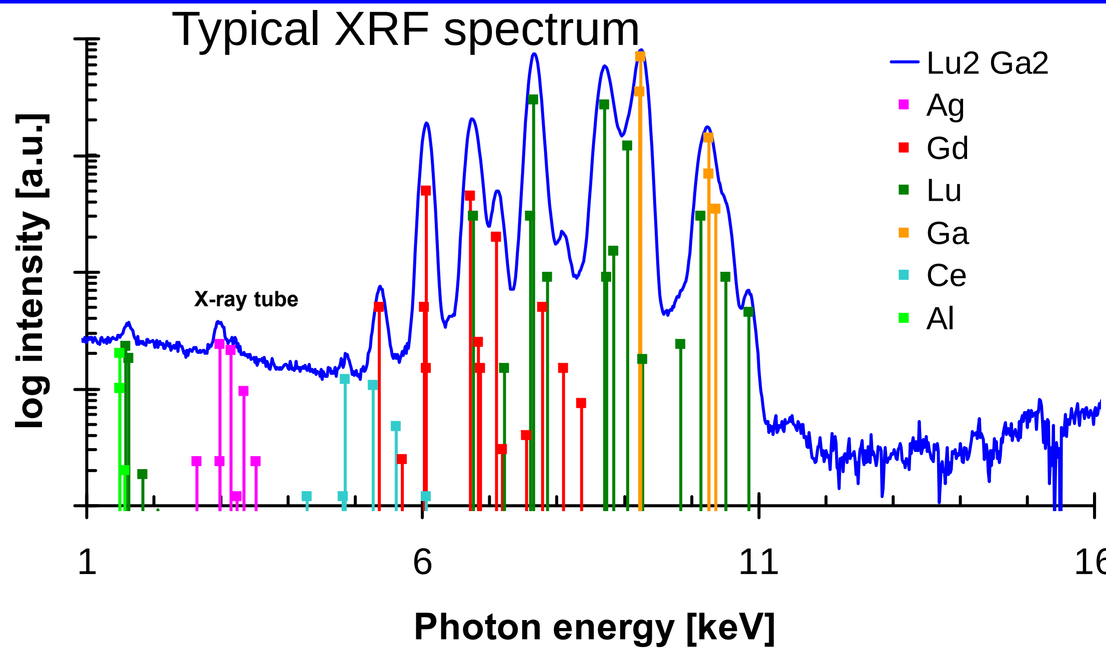
☹ Intensity decrease

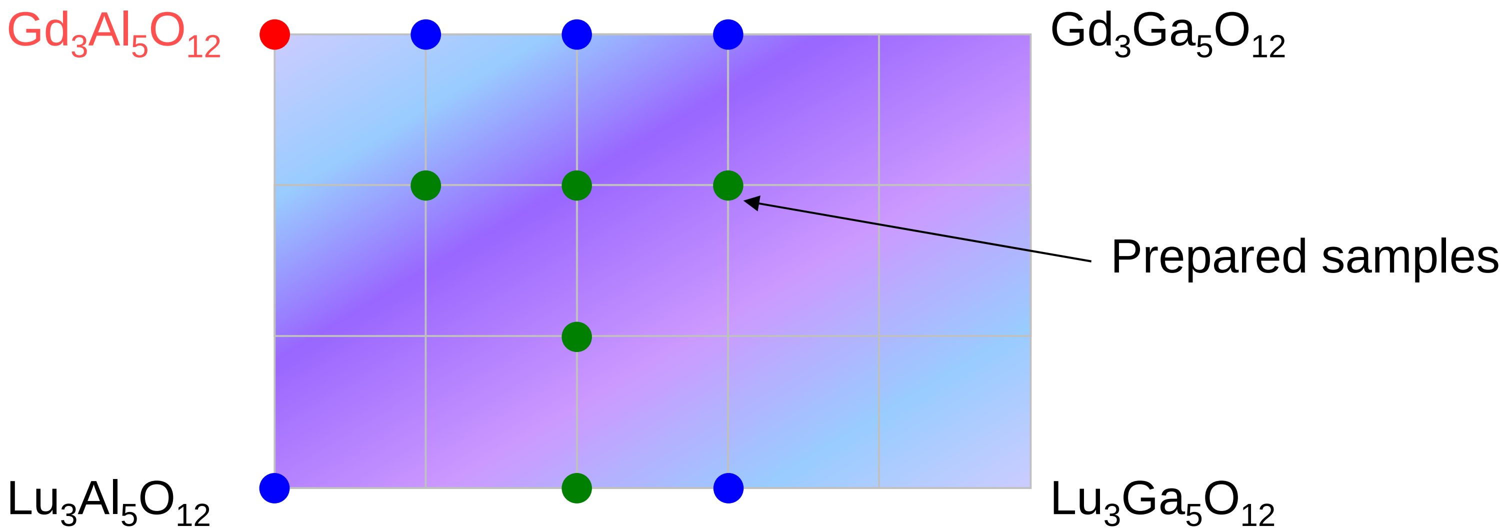
☺ Both Mg and air decrease the decay time

(Bárta et al., 10.1109/TNS.2018.2803278)

GLuGAG – preparation

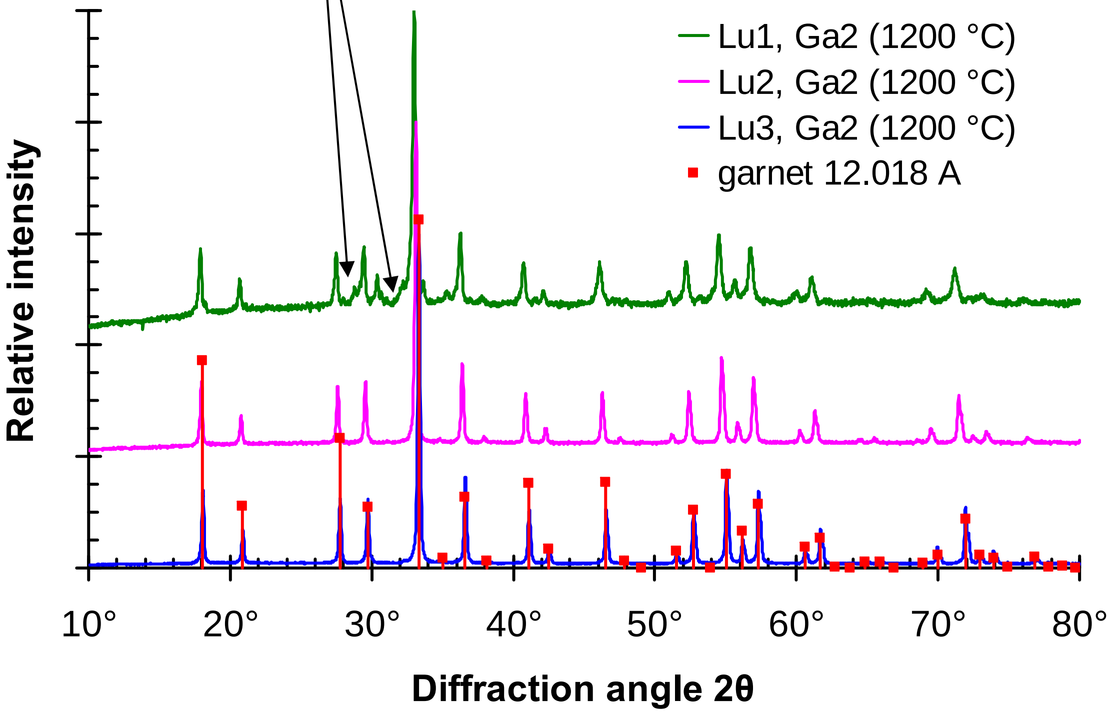
- $(Gd,Lu)_3(Ga,Al)_5O_{12}$
- Complex 2D solid solution
- Usually completely arbitrary integer indices ☺
- Gd shifts Ce^{3+} levels, Ga lowers the conduction band

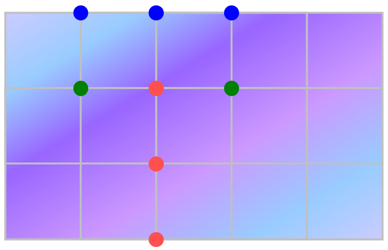




GLuGAG – XRPD (Lu-Gd)

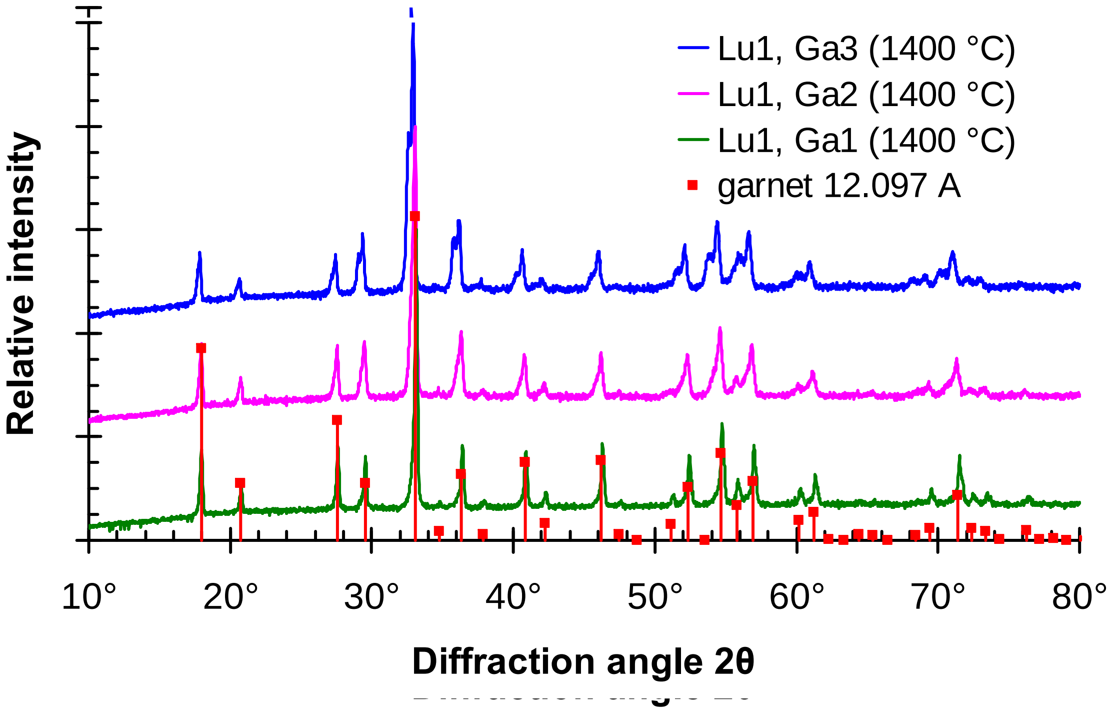
- On the Gd-Lu axis, lattice parameter *a* increases with Gd content (Vegard's law), complies with the theoretical calculation
- Strong fluorescence of Gd in XRPD (Cu-K_a radiation)
- Phase impurities in the $Gd_2Lu_1Ga_2Al_3O_{12}$ composition at 1200°C: GAM, Gd gallate oxide

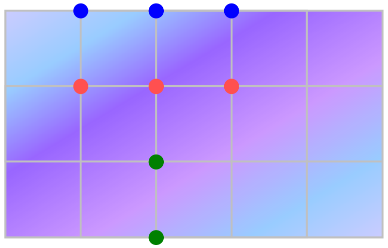




GLuGAG – XRPD (Al-Ga)

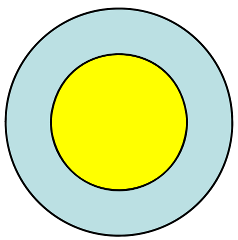
- On the Ga-Al axis, *a* increases linearly with Ga content
- After calcination at 1200 °C, the Gd_2Lu_1 samples contain phase impurities; at 1400 °C, only garnet phases are present
- Two garnet phases or distribution for $Gd_2Lu_1Ga_{2/3}Al_{3/2}O_{12}$ (further heating necessary?)

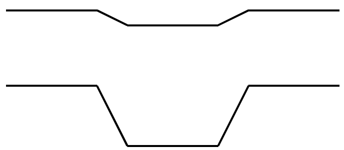




Core-shell garnet structures

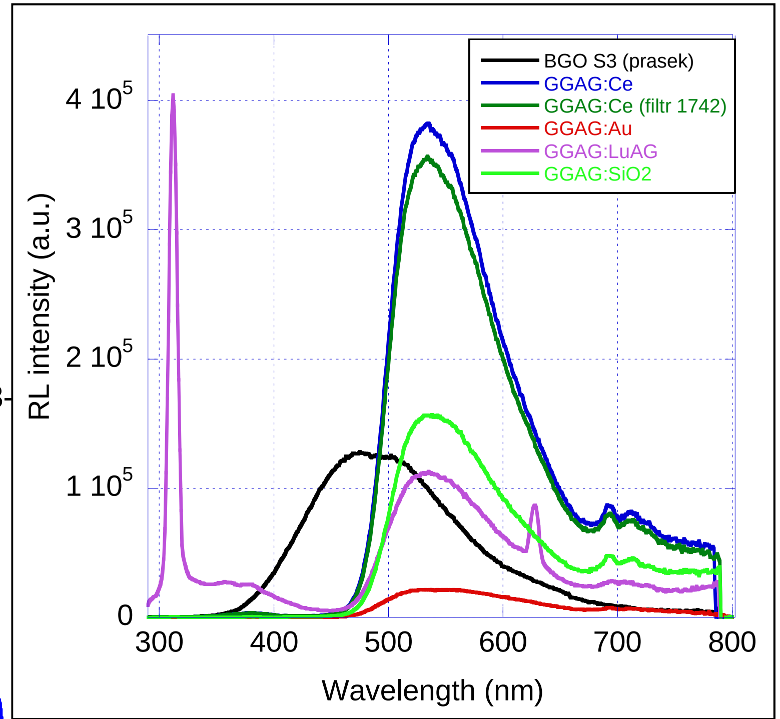
- Idea: to cover a pre-formed garnet core with a shell
  - Elimination of the surface defects
  - Band-gap differences to confine charge carriers in the core
- GGAG:Ce nanocrystals ball-milled to reduce the aggregates
  1. Sol-gel coverage by thick amorphous silica shell (TEOS hydrolysis)
  2. Irradiation of $HAuCl_4$ solution with GGAG particles by UV light to form Au colloid (red)
  3. Irradiation of solution containing Lu^{3+}, Al^{3+}, $HCOO^-$ with GGAG particles and mild heating (1000 °C)

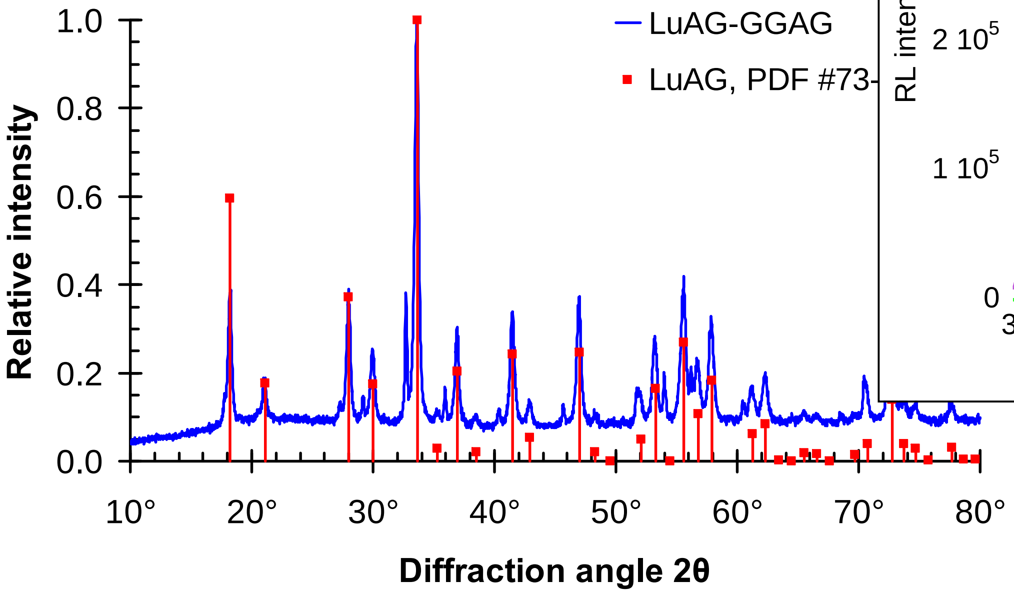




Core-shell garnet structures

- Addition of a shell decreases the luminescence intensity, even with „transparent“ coating
- LuAG coverage of GGAG:Ce using mild calcination caused intergrowth of core and shell (Gd^{3+} emission is quenched in GGAG)
- Au plasmon absorbs the Ce^{3+} emission





Conclusions

- Fast, simple and efficient way to produce garnet nanoparticles
- Multi-component garnets are possible, but sometimes need proper calcination procedure to obtain pure garnet phase
- Thick surface coating (core-shell structure decreased luminescence intensity of GGAG:Ce)