Properties of scintillating nano-oxides
(extrinsic scintillators)

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Extrinsic or intrinsic scintillator?

Extrinsic – emission from luminescence centers

Intrinsic – exciton related luminescence (free exciton, self-trapped ex., self-activation luminescence)

band-to-band absorption and emission

- Wide band gap semiconductors

- In some materials – both types (ZnO:Eu(RE) x ZnO:Ga(La,In); HfO_2:Ti x HfO_2)

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Properties – intro

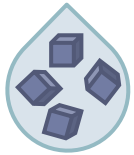
- Properties of nano-oxides are often strongly influenced by their origin; their preparation and treatment thus deserve special attention

SPARTE
Scintillating Porous Architectures for RadioacTivE gas detection

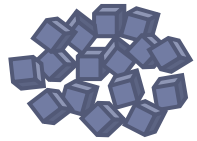
What exactly are the nano-oxides? $MO_x \oplus$ nano

- Nanoparticle:
  - Object with each dimension < 100 nm (arbitrary value), in liquid / free-standing

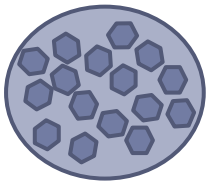
400 nm (purple) light



= colloid



- Nanocrystalline material:
  - Single crystalline domains < 100 nm, particles can be much bigger



- Nanomaterial:
  - Object with at least 1 dimension < 100 nm

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Preparation of nano-oxides

Arbitrarily divided into:

- **„Physical" methods** – large equipment, small amounts can be synthesized, usually „clean"; high-energy milling, spray pyrolysis, deposition from gas (PVD), …
- **„Wet chemical" methods** – formation of solids / colloids in liquids, large amounts can be prepared, some residual chemicals; sol-gel reactions (alkoxide hydrolysis and polycondensation, Pechini method, urea hydrolysis), co-precipitation, …
- **„Combined" methods** – use both physical and chemical aspects; hydrothermal synthesis, solid-state reactions, chemical vapour deposition, radiation & photochemical synthesis, …

- Separation of nano-oxides (sol or gel) from liquids:
  - Filtration / centrifugation and drying – collapsed xerogel, serious agglomeration
  - Freeze-drying of gel (lyophilization) – H_2O sublimes from the frozen gel
  - Super-critical drying – exchange of solvent with super-critical fluid (e.g. CO_2) and its evaporation: the gel does not collapse and aerogels can be prepared

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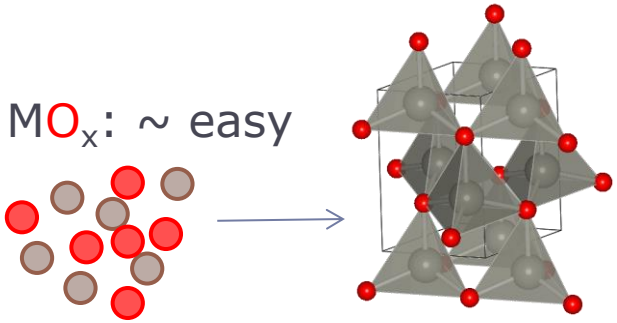
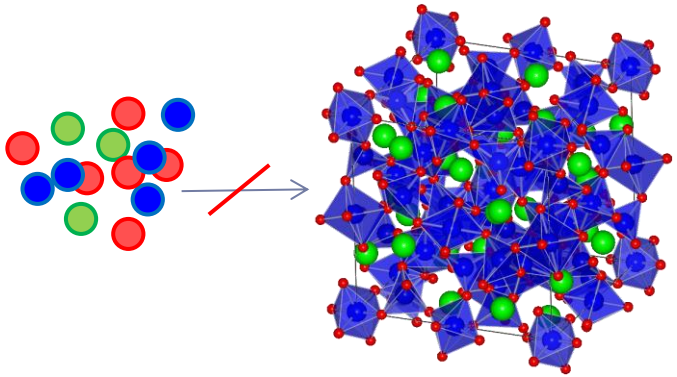
Formation of oxides

- How easily can be oxides *directly* formed by „wet" chemical methods?
- Simple oxides MO_x: ~ easy

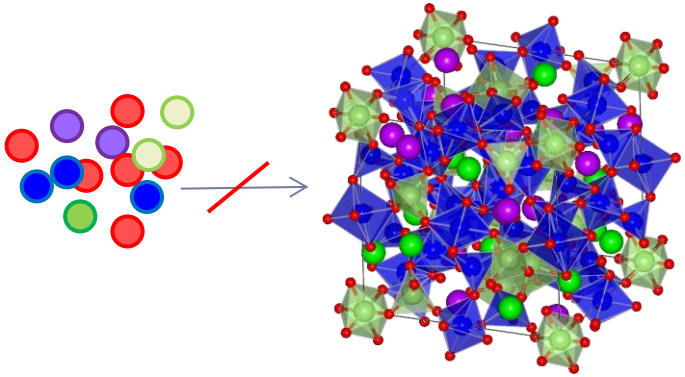


ZnO

- Mixed oxides $(M,M')O_x$ and intricate structural motifs: very unlikely



YAG ($Y_3Al_5O_{12}$), LuAG ($Lu_3Al_5O_{12}$)



$(Gd,Lu)_3(Al,Ga)_5O_{12}$

- Multi-component oxides $R_rS_sT_tU_uO_x$: virtually impossible

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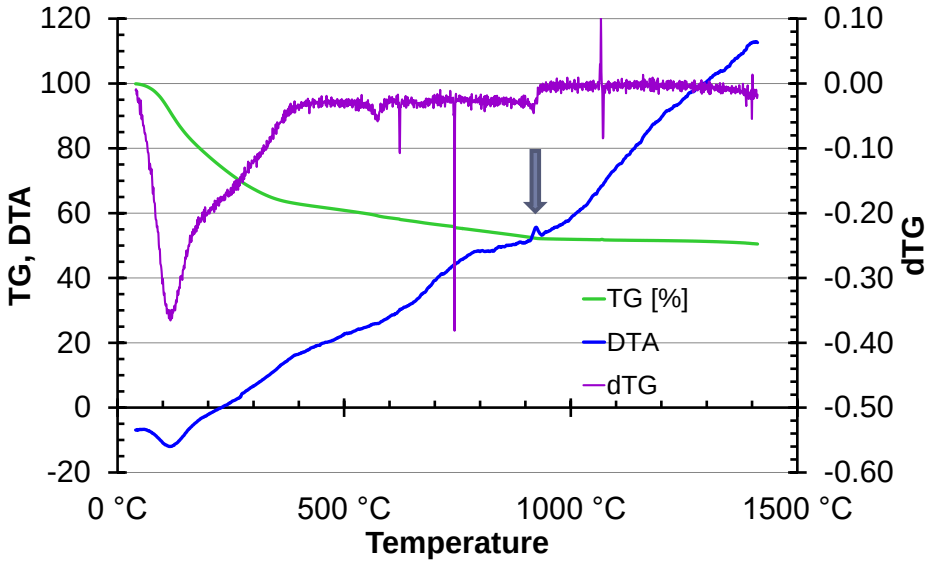
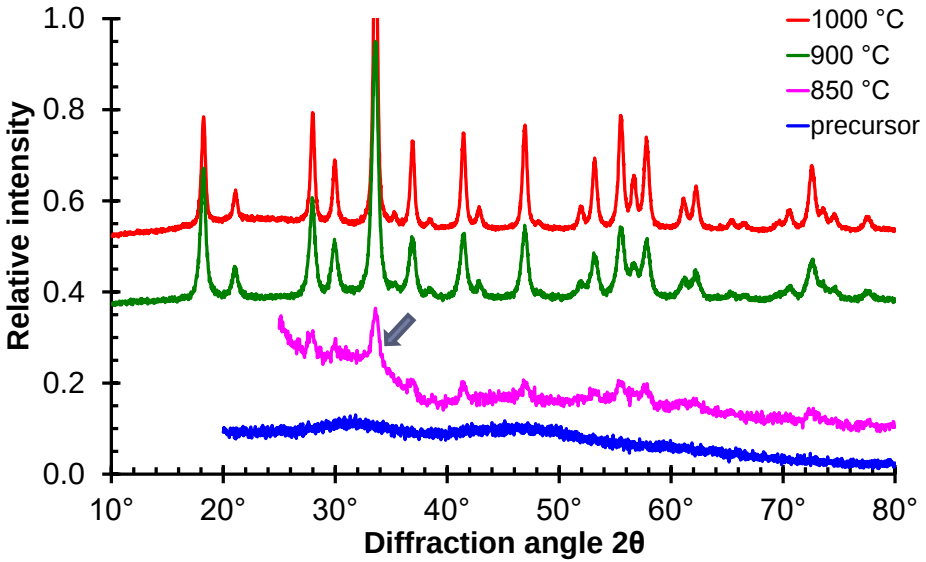
Formation of oxides

- Indirect preparation = *an (amorphous) solid precursor* transforms into ~ thermodynamically stable[1] oxides during heat treatment
- Transition to crystalline oxide is observable by:
  - **DTA** (differential thermal analysis) – exothermic peak
  - **XRD** (X-ray diffraction) – emergence of characteristic reflections
  - **electron microscopy** (TEM) – diffraction fringes / SAED patterns





[1] Phase diagrams should always be consulted: e.g. $Gd_3Al_5O_{12}$ is semi-stable with respect to $GdAlO_3$ + Al_2O_3, while $LuAlO_3$ (or $YAlO_3$ at low temperatures) is unstable with respect to $Lu_3Al_5O_{12}$ + $Lu_4Al_2O_9$ / Lu_2O_3

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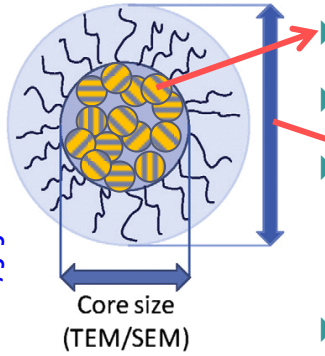
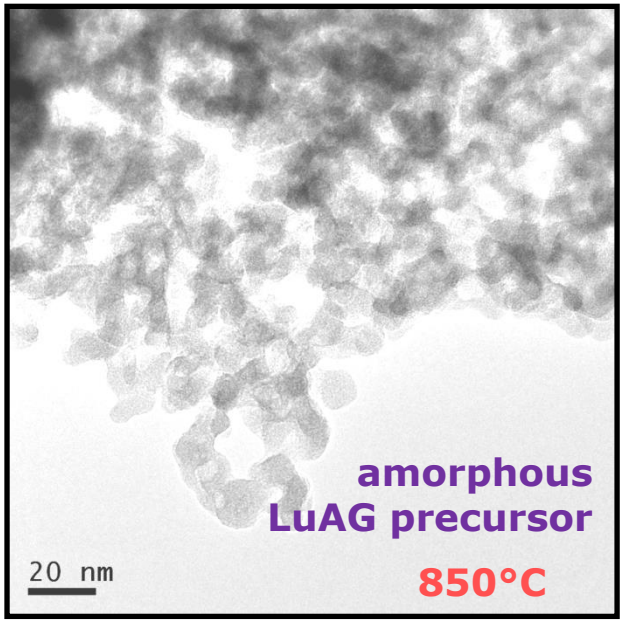
Size of nanoparticles

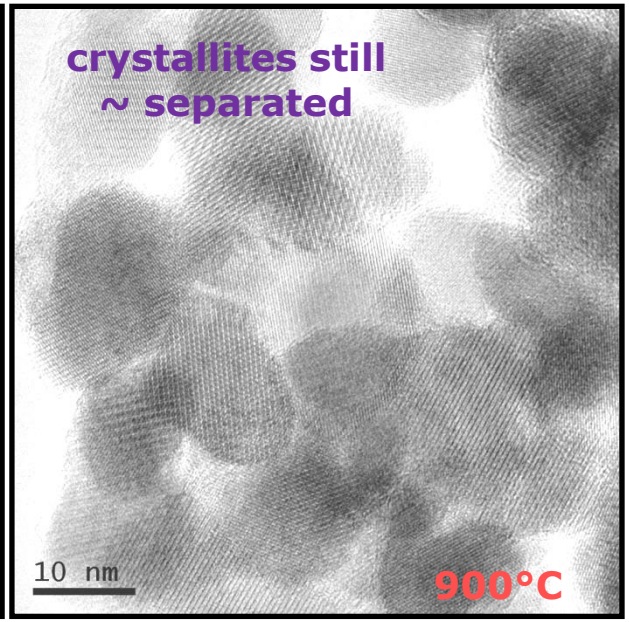
Rabanel et al., 10.1016/j.jconrel.2014.04.017

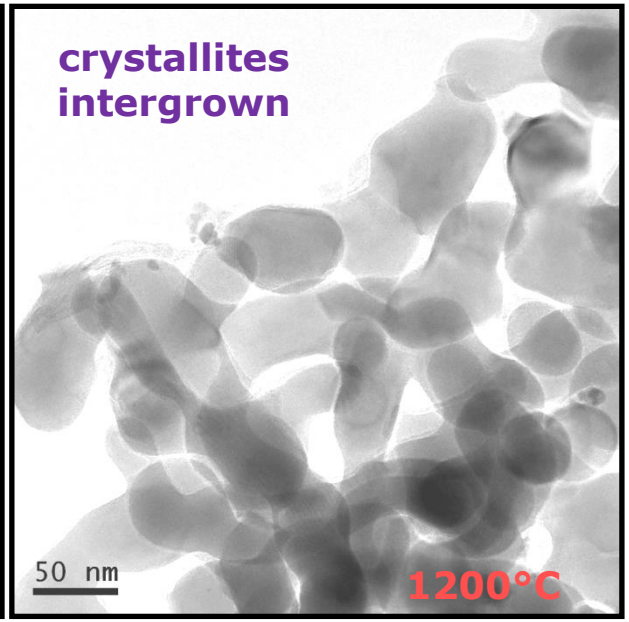


- Crystallite size – XRD (peak broadening), tiny single crystals
- Grain size – SEM / TEM, size of physical objects
- Hydrodynamic diameter – DLS, grain with bound ligands / solvent (not relevant in powders, crucial in colloids)

- Heat treatment of nano-oxides causes coalescence (crystal size growth), necking and sintering (grain size growth)







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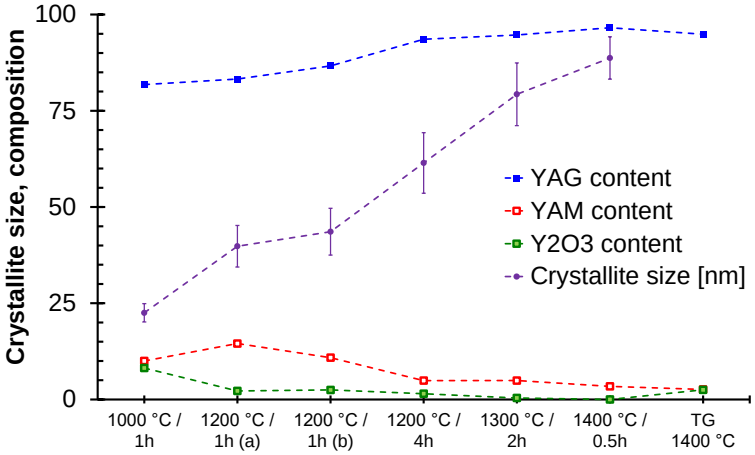
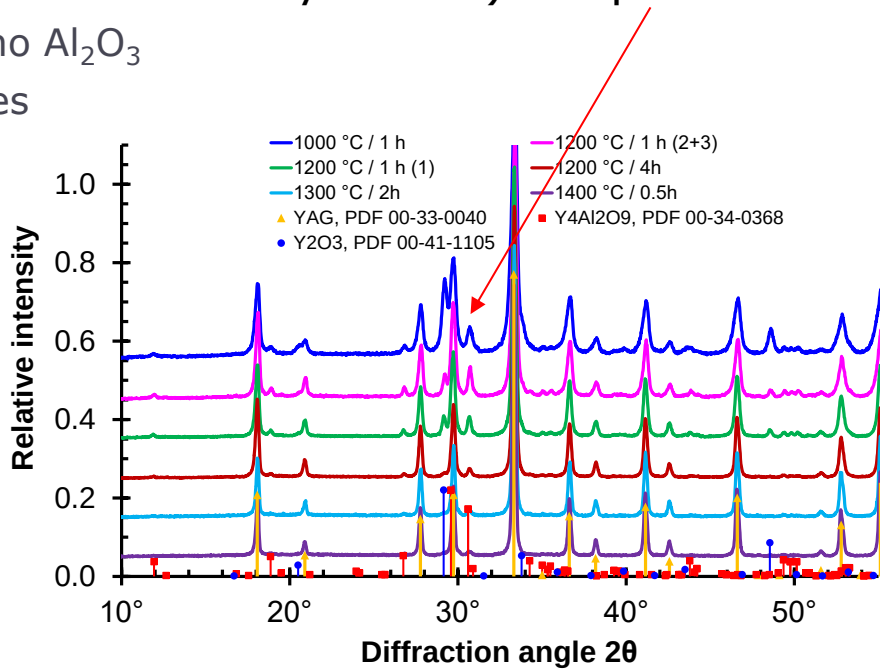
Phase purity

- Calcination / annealing temperature affects nano-oxide composition
- Kinetic aspect – phase changes during YAG synthesis:
  - Inhomogeneous precursor: diffusion-rate controlled process

see e.g. Kupp et al., 10.1557/jmr.2014.224

- XRPD of lyophilised YAG precursor (photochem. synthesis) – 3 phases
  - YAG ($Y_3Al_5O_{12}$) + Y_2O_3 + YAM ($Y_4Al_2O_9$), no Al_2O_3
  - The phase composition markedly improves with dwell time and temperature of annealing → *Kinetic* issue (diffusion)





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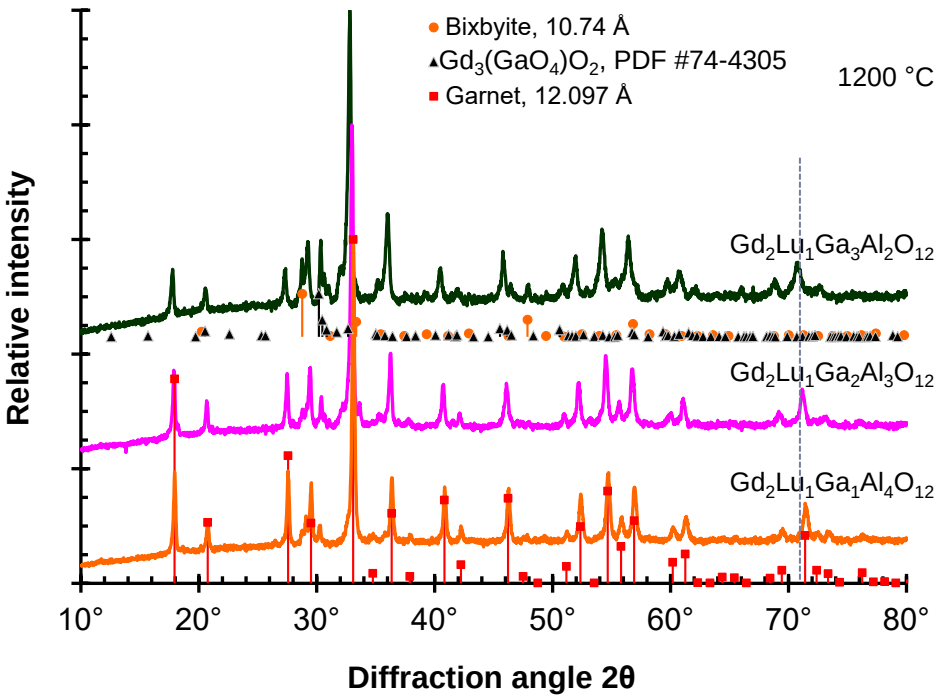
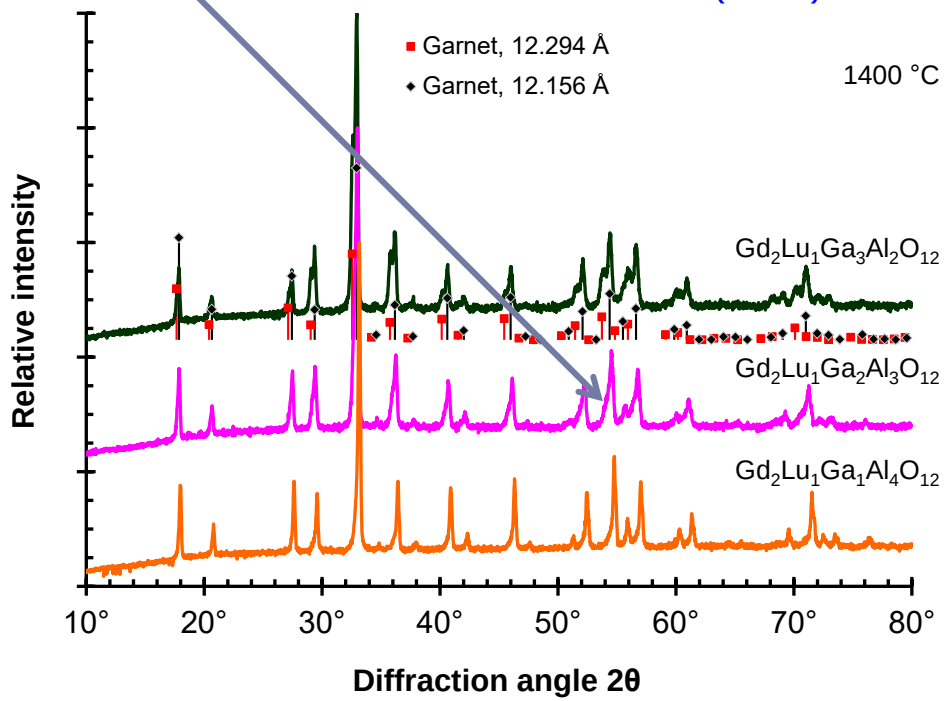
Phase purity

- Multi-component oxides require annealing at very high temperatures to achieve phase-pure materials
  - $(Gd,Lu)_3(Ga,Al)_5O_{12}$:Ce achieved „phase purity" after 1400 °C
  - Doubling of diffraction peaks / tail toward low 2θ = not a single garnet phase; improvement possible by longer annealing / higher temp.

Bárta et al., Radiat Meas (2019) 124:98





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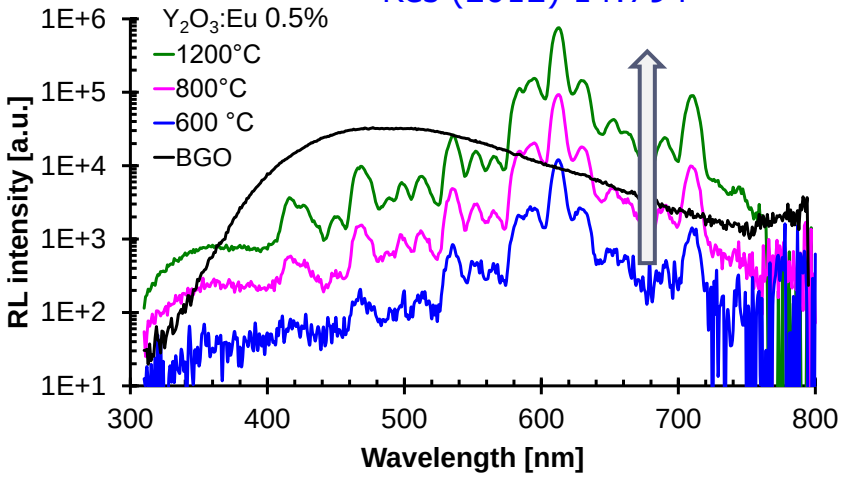
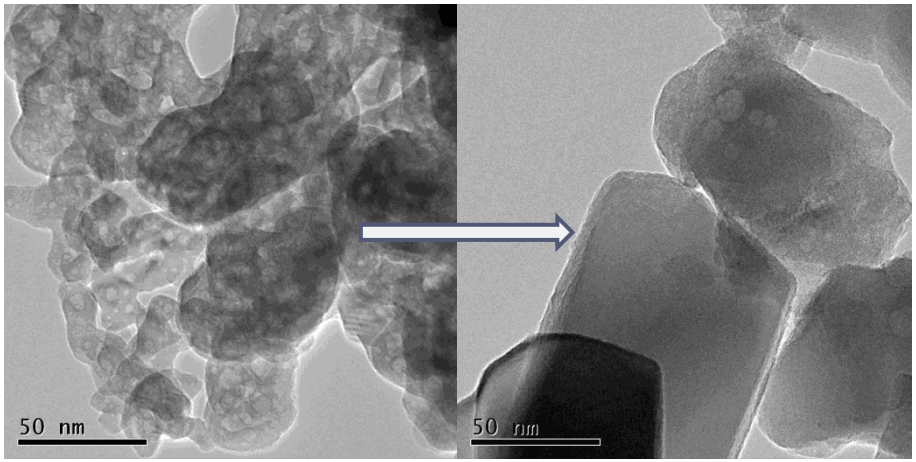
Annealing effects

- Luminescence intensity of dopant's emission usually increases with annealing / calcination temperature
  - ☺ Healing of structural / surface defects decreases the density and efficiency of traps
  - ☹ Particle size increases with temperature
  - ☹ Some dopants / matrix elements can change their oxidation states ($Ln^{3+} \rightarrow Ln^{4+}$ when annealed in air: Ce, Pr, **Tb**)
  - ☹ Some oxides can be volatilized (Ga_2O_3, SiO_2, Sb_2O_5)

Y_2O_3:Eu

Čuba et al., J Nanopart Res (2012) 14:794





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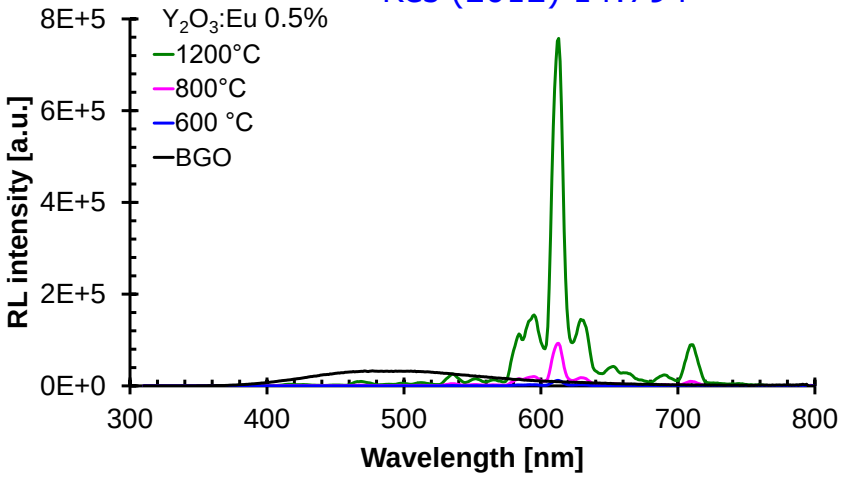

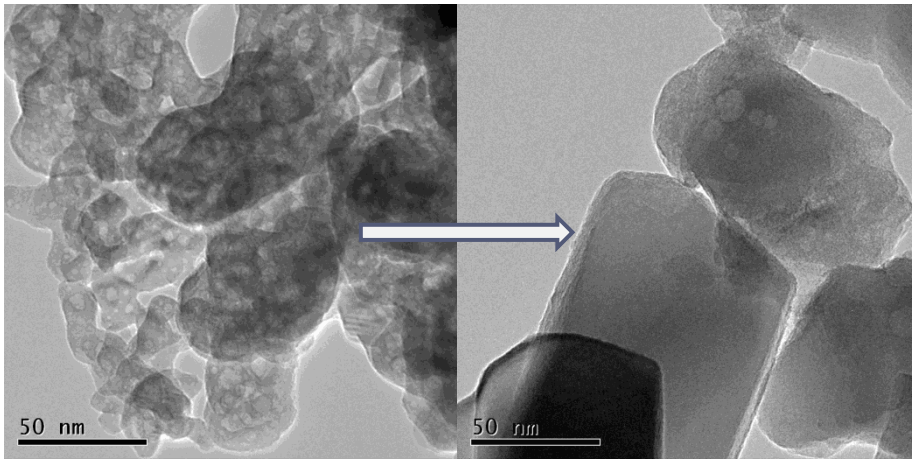

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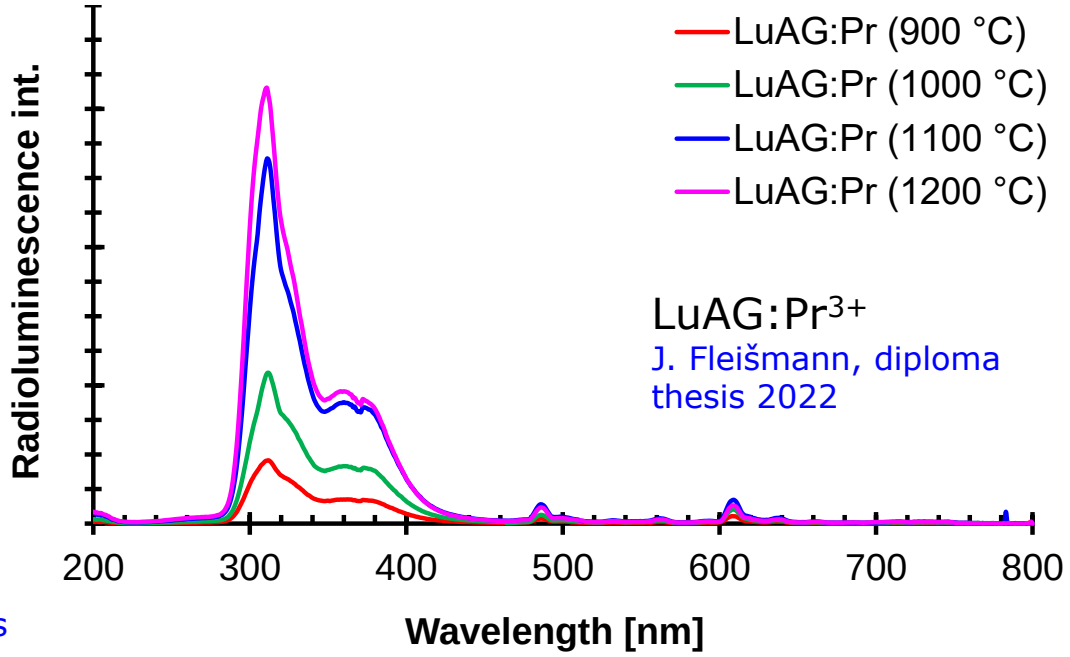
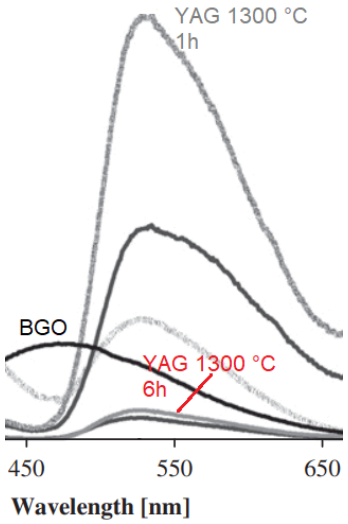
Annealing effects

- RL emission intensity of most extrinsic nano-oxide scintillators increases with annealing time or temperature
- Decrease at some point is probably connected with some adverse effect



LuAG:Pr^{3+}
J. Fleišmann, diploma thesis 2022



YAG:Ce (Cr,Gd)
Čuba et al., Radiat Phys Chem (2011) 80:957

Prolonged heating at 1300 °C in air oxidized most of Ce^{3+}, in this case it led to a low RL intensity

TAG:Ce ($Tb_3Al_5O_{12}$)
J. Indrei, dissertation 2022

Heating of TAG in air caused grey colouration and very low RL intensity (TbO_{2-x} is black)

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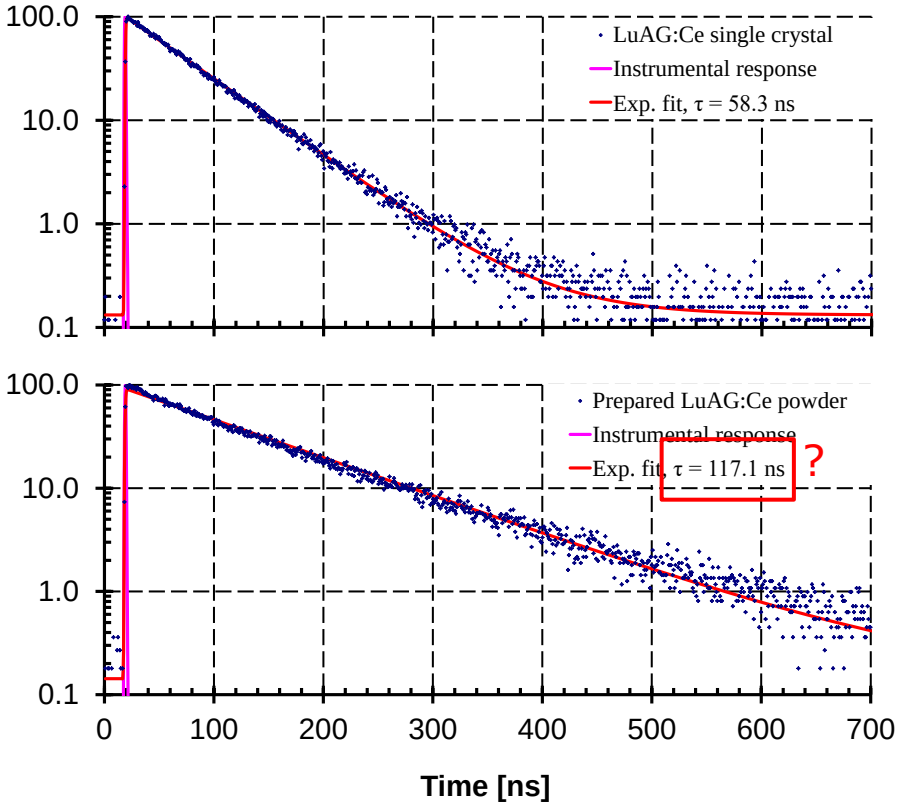
Other effects of nano-scale

- In many garnet-based nano-oxides, the observed decay times of dopants‘ photoluminescence (such as Ce^{3+} or Pr^{3+} $5d-4f$) were longer than in single crystals
  - Parasitic processes always decrease the PL decay times



LuAG:Ce photoluminescence

Bárta et al., J Mater Chem (2012) 22:16590

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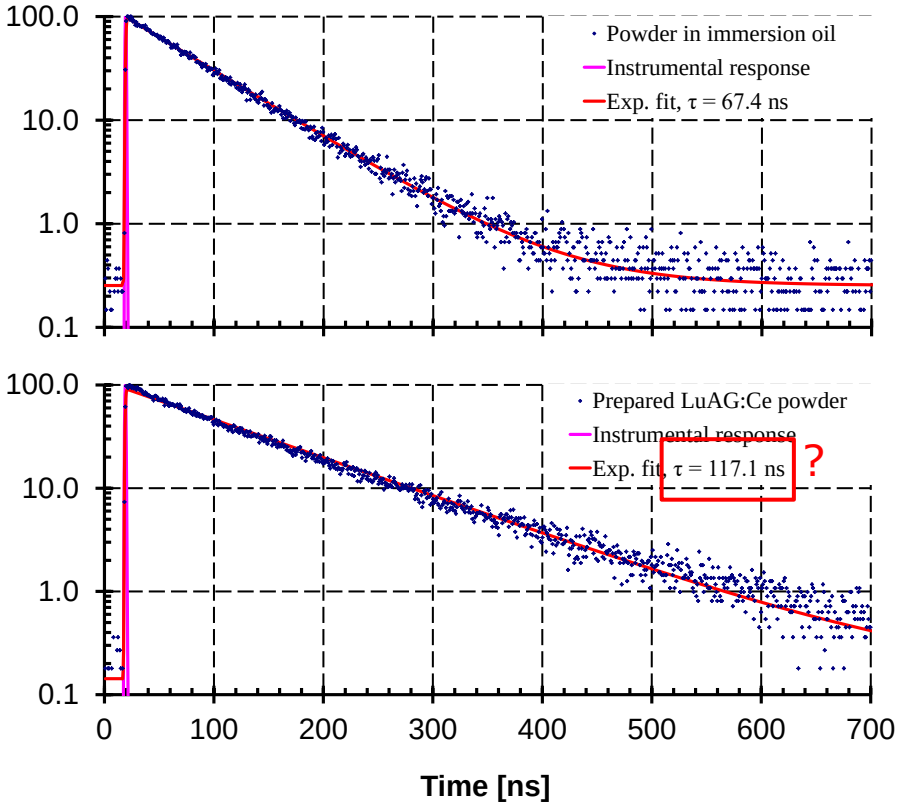
  - Parasitic processes always decrease the PL decay times
  - The emission rate is known to depend on refractive index *n*

  Dujardin et al., IEEE Trans Nucl Sci (2010) 57:1348
  - Nanoparticle perceives *n* from itself and the surrounding medium

$$\tau_r \propto \frac{{\lambda_0}^2}{f \cdot (n^2+2)^2 \cdot n}$$

Di Bartolo, Optical Interactions in Solids, 1968, pp. 403–414.

- n_{LuAG} = 1.84, n_{medium} = 1 … 1.52 calculated filling factors of 58 to 77 % in original samples (2012)



LuAG:Ce photoluminescence

Bárta et al., J Mater Chem (2012) 22:16590

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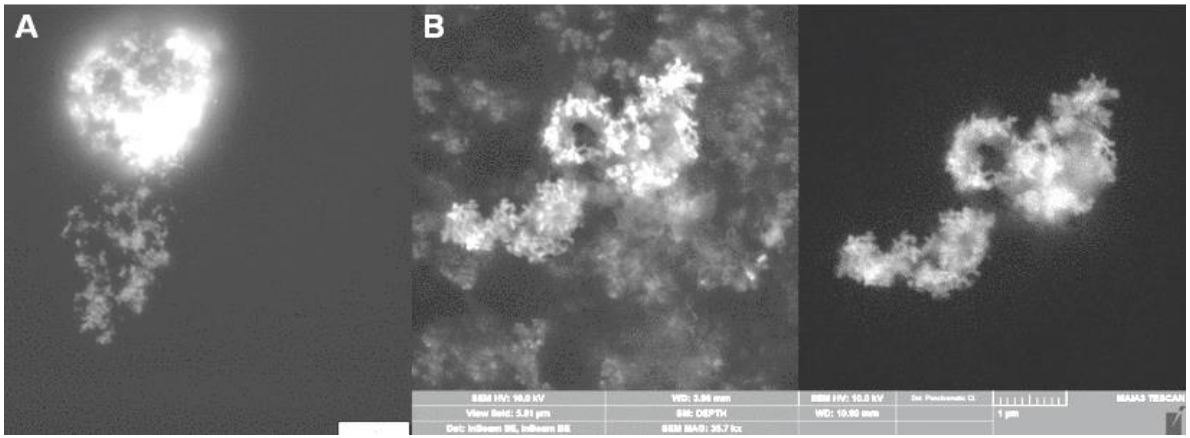
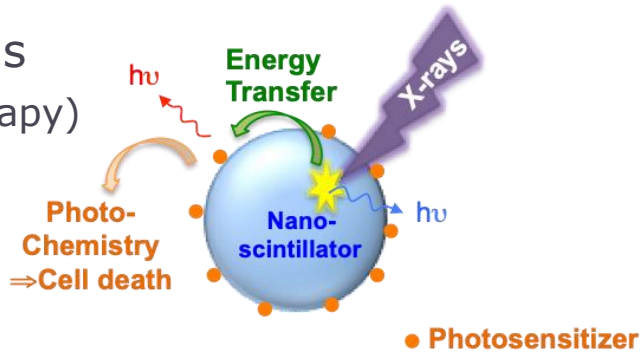
Possible applications

- Nanoparticle cores for bio/medical applications
  - PDTX conjugates (X-ray induced Photodynamic Therapy)
  - Cathodoluminescence imaging

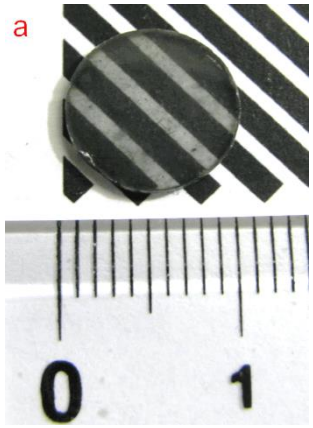




LuAG:Ce & lymphocytes
Popovich et al., IEEE TNS (2020) 67:962

- Precursors for transparent ceramics fabrication

LuAG Spark Plasma Sintering
Pejchal et al., Opt Mater (2016) 53:54



- Precursors for aerogels

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Thank you for your attention!

Next: Lenka Prouzová Procházková (intrinsic scintillators)

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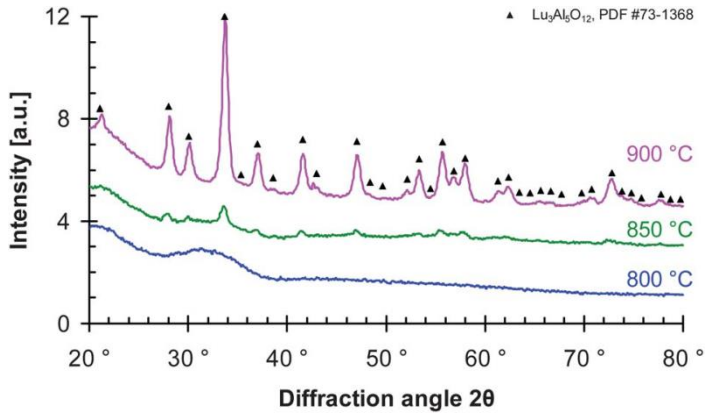
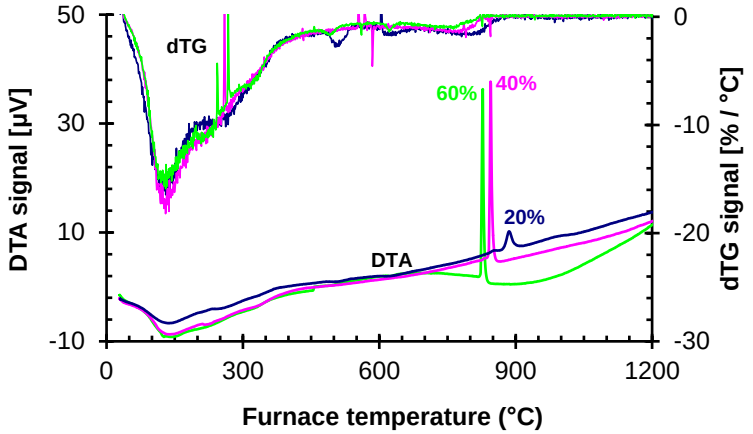
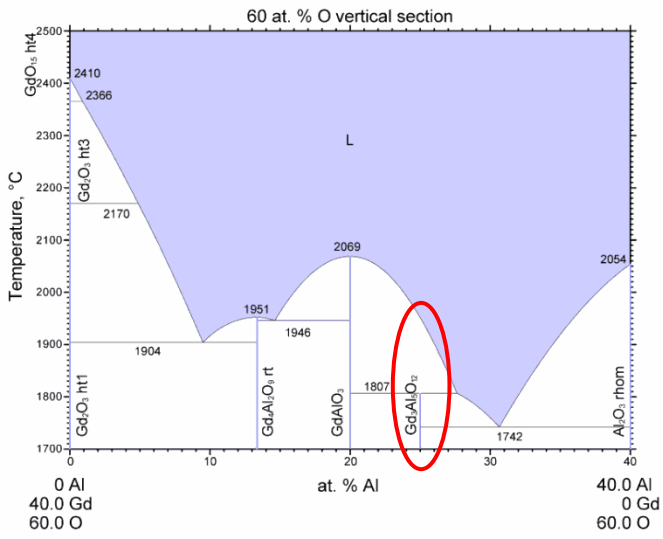
Supporting

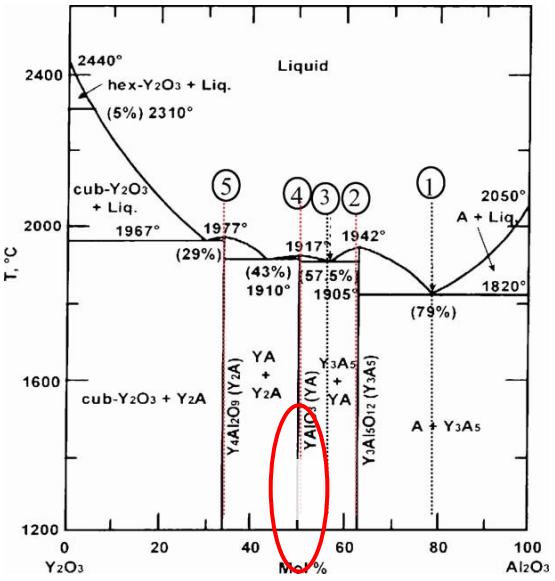


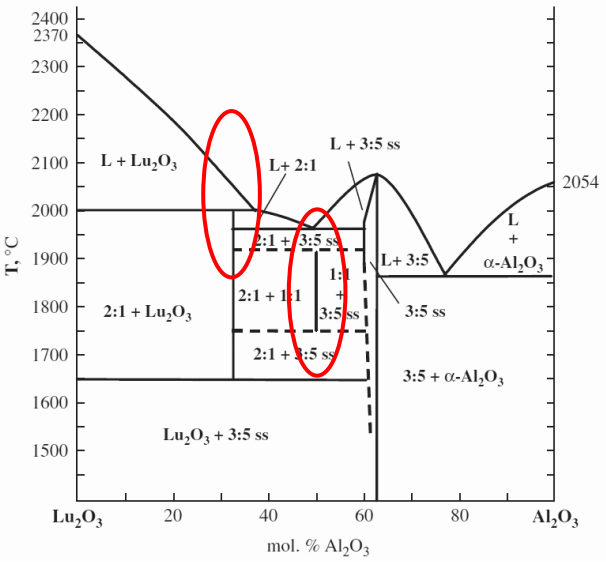
LuAG - 10.1039/c2jm32766j



GGAG - 10.1109/TNS.2018.2803278







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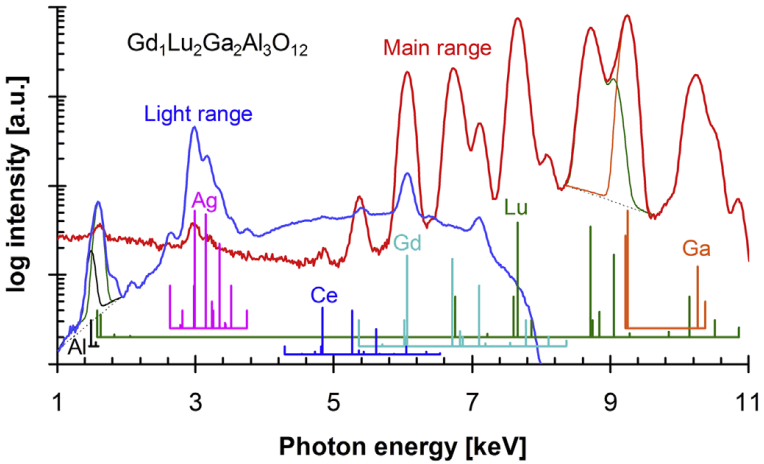
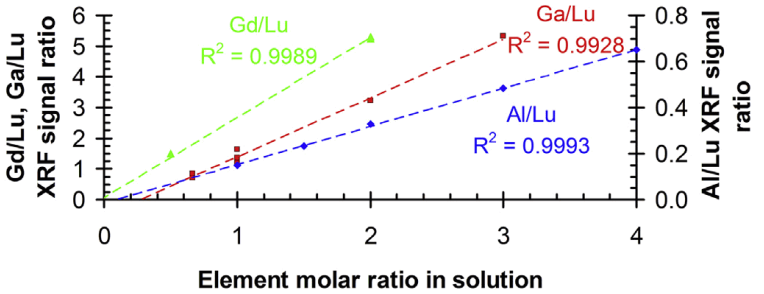
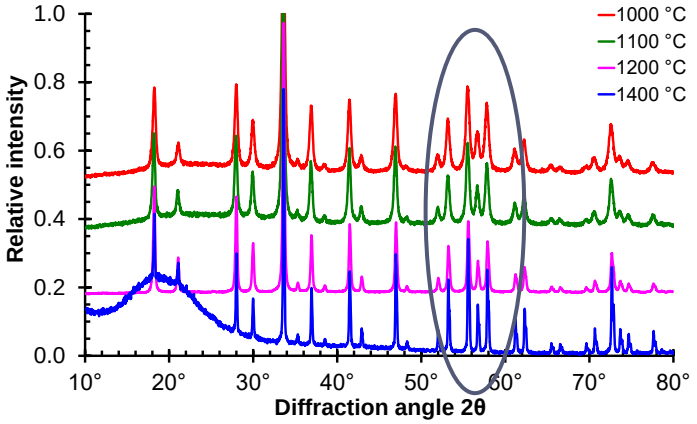
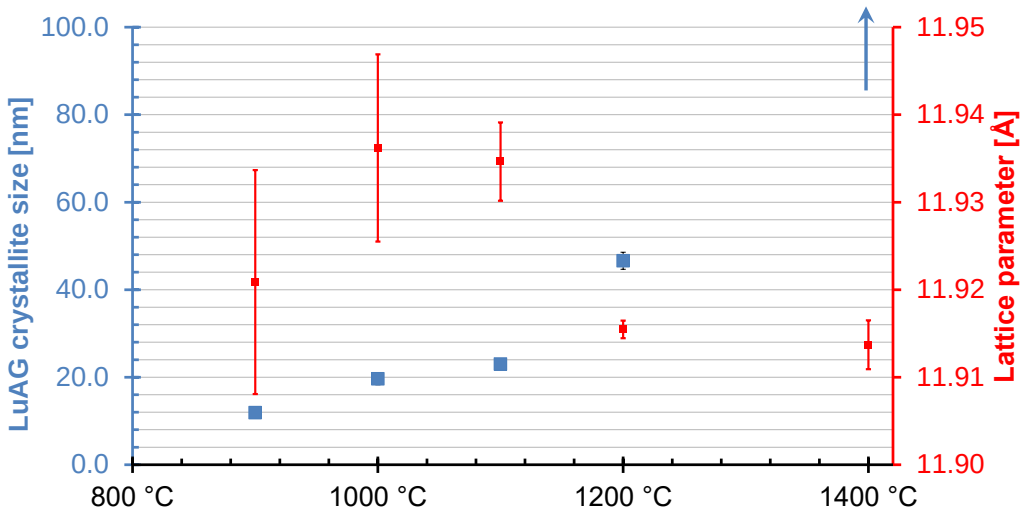




GLuGAG - 10.1016/j.radmeas.2019.03.012





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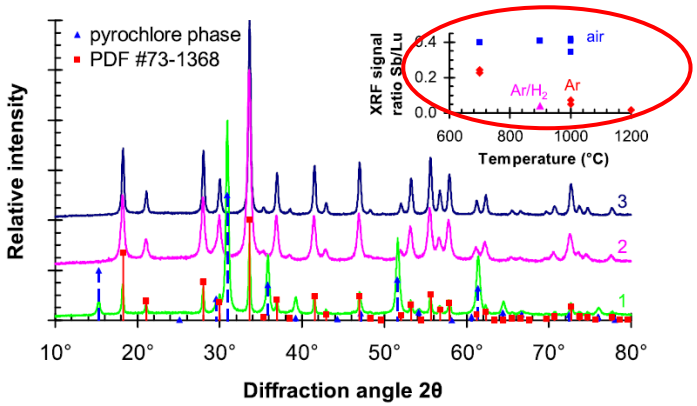
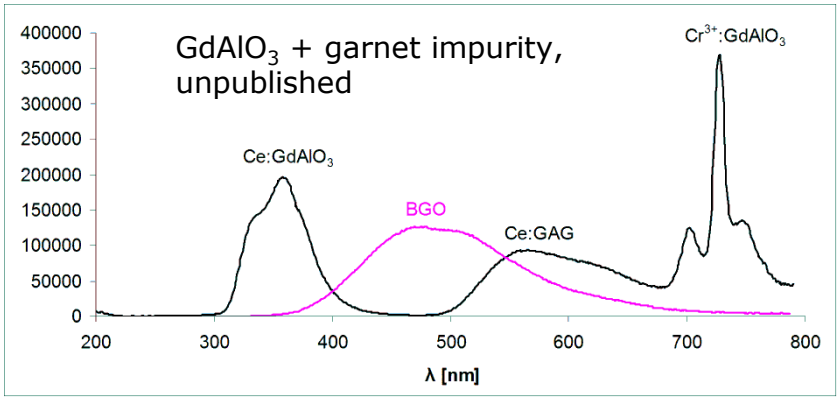
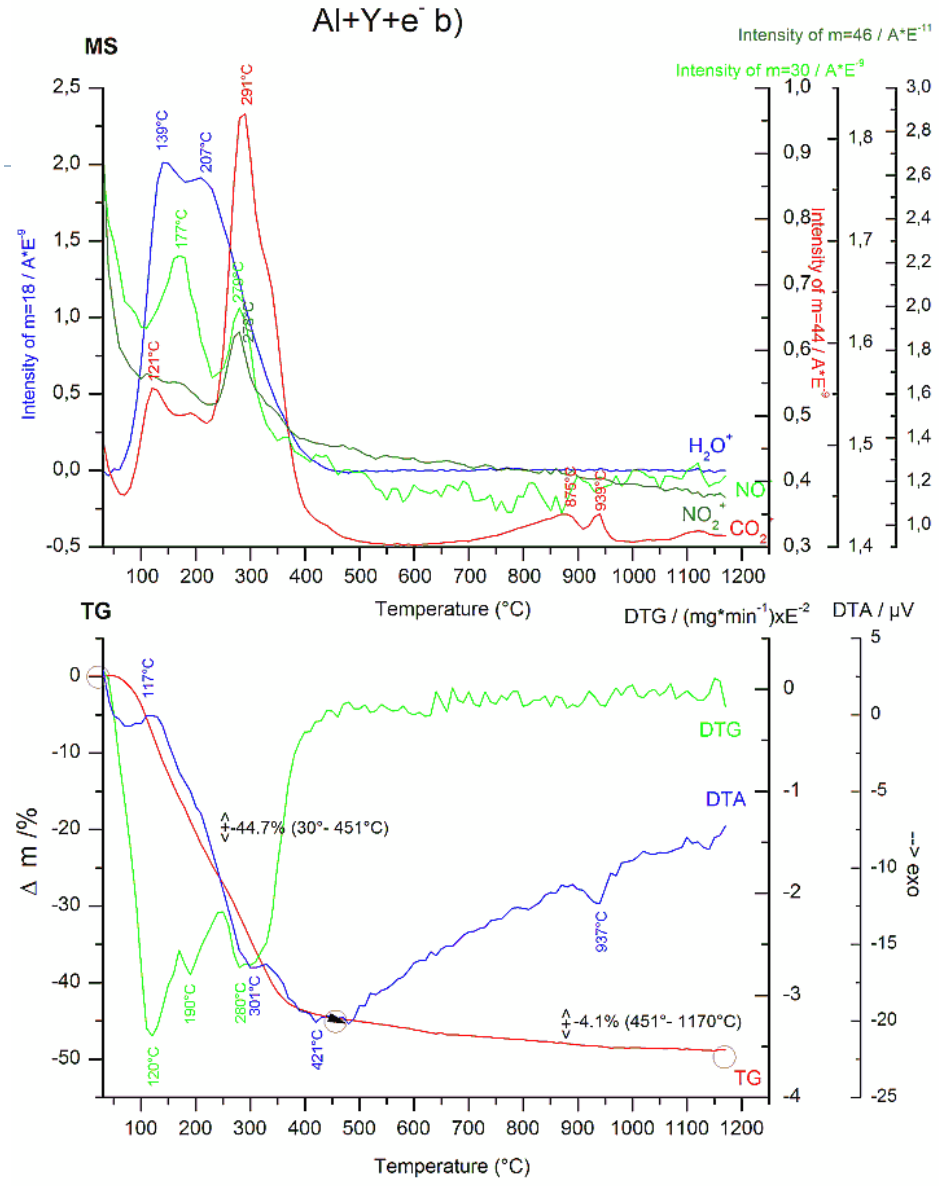


Fig. 6. Diffraction patterns of LuAG:Sb,Eu powders calcined at different conditions (1–1000 °C/2 h/air; 2–700 °C/3 h/Ar; and 3–1000 °C/Ar) compared to the ICDD PDF-2 database record of LuAG and a simulated pyrochlore-type phase with $a = 10.014$ Å. Inset: XRF signal intensity ratios between Sb and Lu for LuAG:Sb,Eu samples calcined at different temperatures in air, Ar or Ar/10% H_2.

LuAG:Sb,Eu - 10.1109/TNS.2018.2803278





YAG:Ce – Čuba et al., 2011

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Supporting

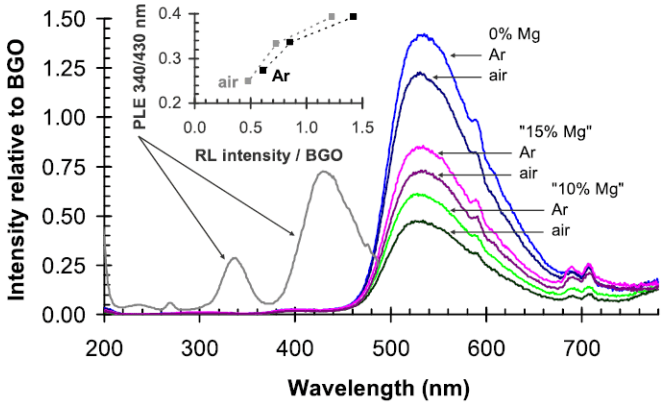


Fig. 4. RL spectra of GGAG:Ce,Mg powders calcined in air or Ar (1500 °C; 10 °C/min; no dwell time) relative to powder BGO emission intensity. Weak

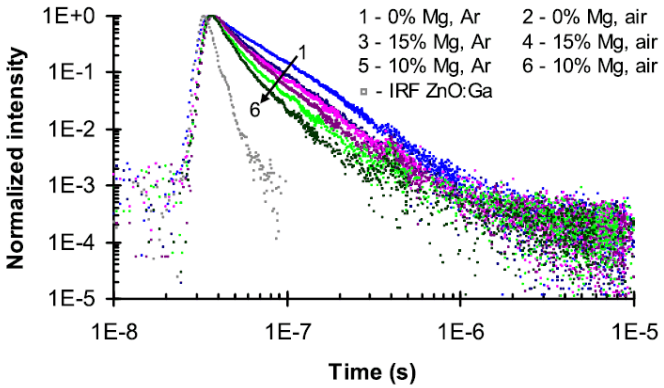
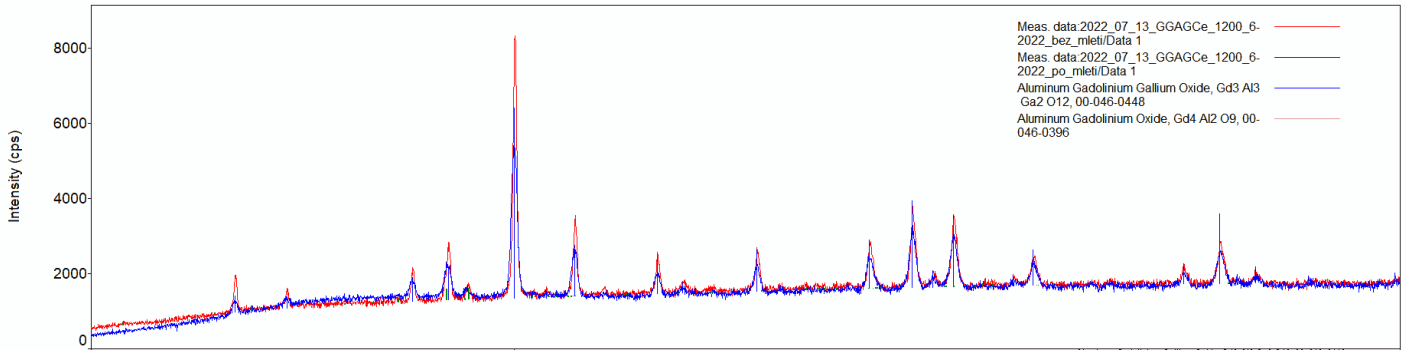


Fig. 5. SXR scintillation decay curves of GGAG:Ce,Mg powders compared to the IRF, (decay of ultrafast ZnO:Ga scintillator). The peak at ~390 ns is an instrumental artifact.

GGAG:Ce,Mg - 10.1109/TNS.2018.2803278



Before milling	GGAG	
s =	0.012	0.036
a =	12.247 Å	0.006 Å
Size [nm]	56.9	9.8
Strain	-	-

After milling	GGAG	
s =	-0.077	0.053
a =	12.240 Å	0.010 Å
Size [nm]	28.4	3.0
Strain	-	-

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