Czech Technical University in Prague

ASCIMAT School on Advanced Scintillator Materials

Radiation synthesis of scintillating nanomaterials

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What is the radiation synthesis?

- The method for preparing nanocrystals from solutions with low amount of defects and narrow size distribution
- Nucleation / formation of solid phase initiated by the energy of radiation

What types of radiation can we use?

- Ionizing radiation (IR) – usually gamma radiation, accelerated electrons
- UV/VIS – UV lamps, lasers, diodes…

Radiation chemistry and Photochemistry

- What is the relation of Radiation chemistry and Photochemistry?
  - There is no clear boundary between the two
  - Photochemical reactions used since the Bronze age
  - 18th century, C.W. Scheele – light sensitivity of silver halides
  - Photochemistry typically deals with the chemical effects of visible or UV light
  - Radiation chemistry established during the Manhattan project
  - Radiation chemistry studies the chemical effects of energetic photons/gamma, but also the other energetic particles

Ionizing radiation

- **What is ionizing radiation (IR)?**
- All types of radiation, ***capable*** to induce ionized (*positive ion – electron* pairs) states in the irradiated medium
- Part of the energy is ***always*** spent in the formation of excited states – non-dissociated, higher then ground energy
- α, β-, β+, γ, accelerated ions, …

Ionizing radiation – chemical effects

- Particles of ionizing radiation impart high amount of energy to the molecules of irradiated medium

- Typical ^{60}Co irradiator emits electromagnetic rays of energy 1.17 and 1.33 MeV

- However, the typical dissociation energy per chemical bond is up to 5 eV

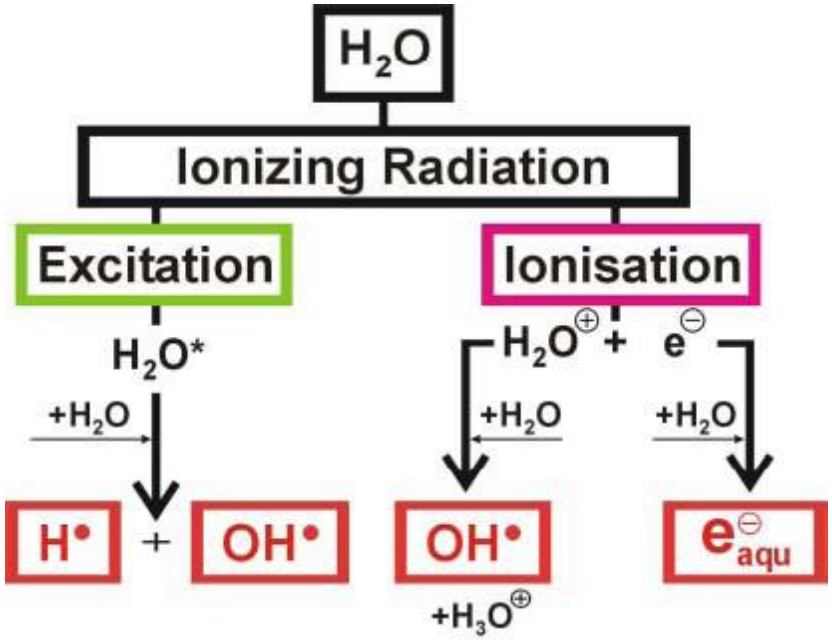
Principles I:

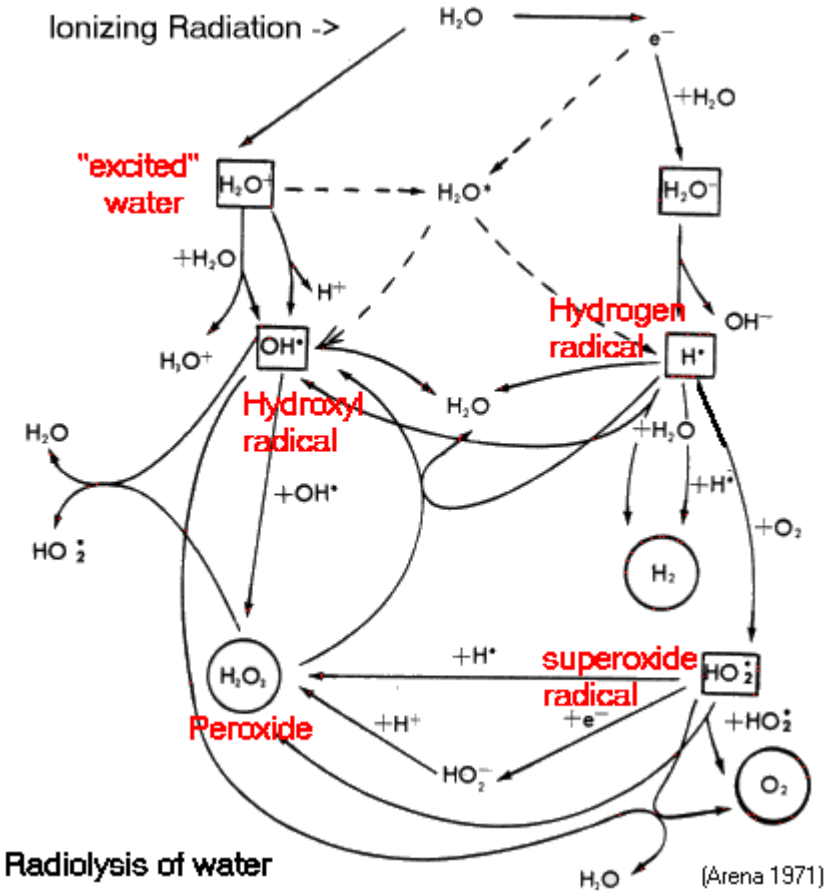
Radiolysis

Radiolysis: important considerations

- **What is Radiolysis?**
  - ***Dissociation of matter by ionizing radiation***
  - ***Splitting chemical bonds***
- LET, dose and dose rate
- Direct and indirect effects of IR
- **Radiation chemical yields**
- **Reactive intermediates**

Water radiolysis: diagram





Three „fast“ stages of radiolysis
1) Physical stage

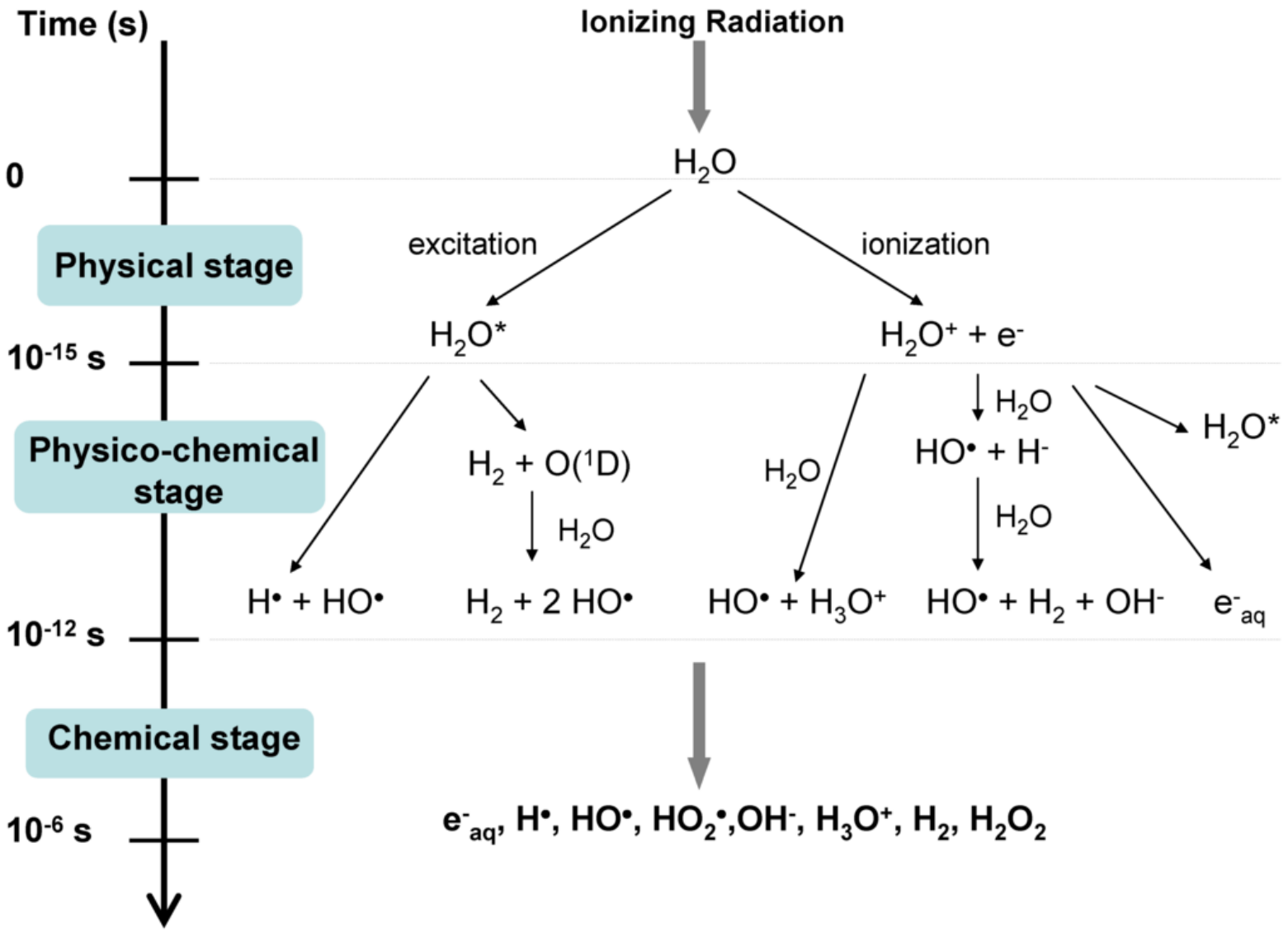
- 10^{-18} *s* – inelastic collisions of light charged ionizing particles (*electrons*) with molecules of environment
- 10^{-17} *s* – inelastic collisions of heavier charged particles with molecules of environment
- 10^{-16} *s* – generation of secondary electrons (*especially true if neutral particles are primary source of radiation*). Energy imparted to the matter transforms to localized or collective electronic excitations
- 10^{-15} *s* – Clear differentiation of the states of individual electrons. First resonant transmissions of the energy. Secondary electron excitations (*liquid*).

2) Physico - chemical stage

- 10^{-14} *s* – Iontomolecular reactions, dissociations of excited molecules (i.e. ionizations). Transformation of electron excitation energy to vibration energy. Epithermalization of electrons.
- 10^{-13} *s* – Gradual thermalization and hydratation of free electrons. Recombination of free radicals in „radical traps“. Internal conversion of excited states (*resulting in less energetic states*).
- 10^{-12} *s* – Translation motion of heavy particles. Degradation of energy to vibration and rotation motion. Beginning of the diffusion of radiolytic products, initial chemical reactions.

3) Chemical stage

- 10^{-11} *s* and more - Chemical reaction of hydrated electrons, diffusion and reactions of metastable molecules and transition products in the chemical tracks; transition products of radiolysis diffuse further to irradiated medium (borders of the track are breached) – dissipation of energy. Luminescence, reactions of valency triplets and high Rydberg states.
- 10^{-6} *s* – 10^{-3} *s* – End of chemical processes, possible beginning of biochemical and biological processes.



S. Le Caer, 2011

Principles II:

Tracks of ionizing particles

Water radiolysis: formation of primary intermediates

- Ionization of water leads to formation of ion pair:
  $\mathbf{H_2O \rightarrow H_2O^+ + e^-}$
- Subsequently, OH radicals are formed:

  $\mathbf{H_2O^+ + H_2O \rightarrow H_3O^+ + \cdot OH}$
- Coincidental excitation of water molecules leads to the formation of hydrogen and hydroxyl radicals:

  $\mathbf{H_2O \rightarrow H_2O^* \rightarrow \cdot H + \cdot OH}$

Water radiolysis: formation of primary intermediates

- Genesis of hydrated electrons:

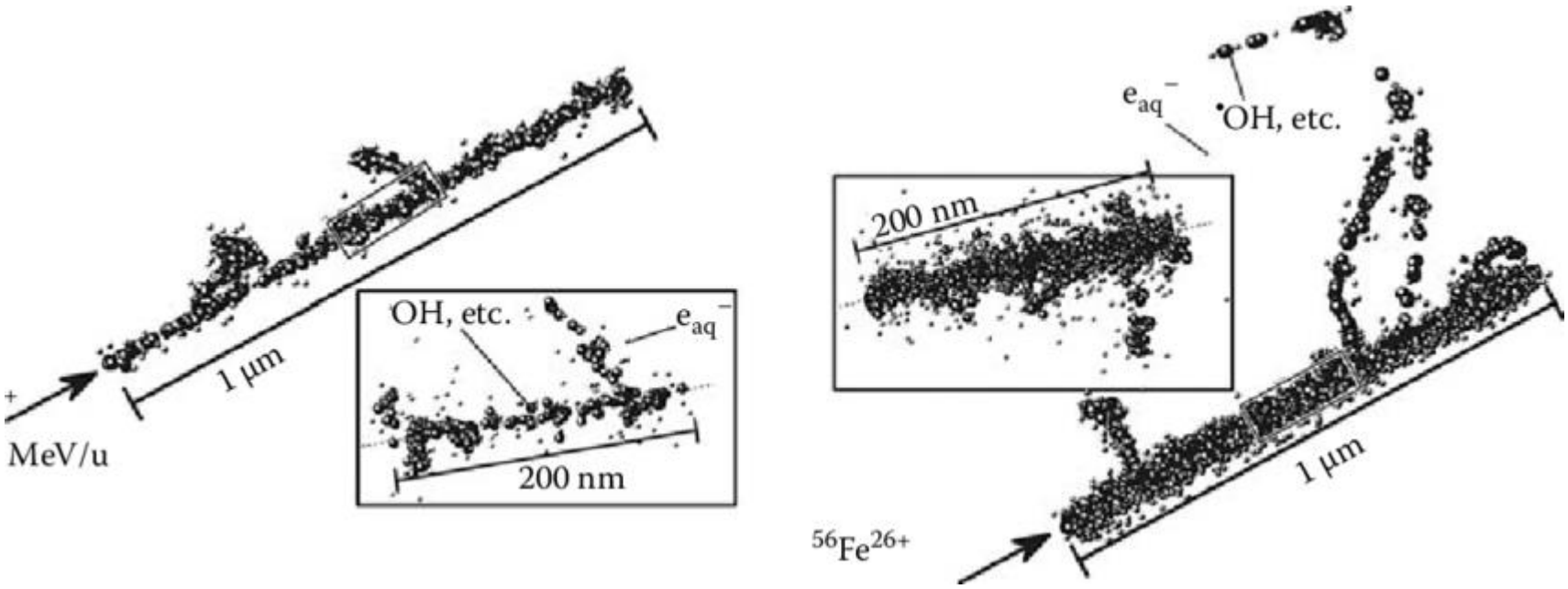
  $e^- + nH_2O \rightarrow e^-_{aq}$

- In acidic environment, hydrogen radicals may be generated via reactions of electrons:

  $e^-_{aq} + H_3O^+ \rightarrow \cdot H^p + H_2O$

- Other important reactions:

  $\cdot H + \cdot H \rightarrow H_2$; $\cdot OH + \cdot OH \rightarrow H_2O_2$



Example of a track of ionizing particle (heavy ion) in liquid water

Yamashita et al. 2010

Water radiolysis: kinetics of products formation

- General formula: $n_x = G(X).D.m = G(X).D.\ \rho\ .V$;

Bodenstein law of stationary concentrations:

Establishing of equilibrium in irradiated matter

Conditions:

- Product forms from the reactive intermediates; rate of ***formation*** of these intermediates is constant
- Rate of termination of intermediates is also constant
- Rates of the formation and termination of intermediates are equal
- Products form with constant rate

Radiostationary state:

- Establishing of chemical equilibrium under constant flow of IR particles (or UV photons).

Water radiolysis: fundamentals of diffusion kinetics

- Reactions of first and second order
- Rate of reactions of molecules with radiolytic products is determined by the slowest step – *diffusion*.
- Diffusion coefficient
- Two approaches: reactions in stationary *x* dynamic system
- Radiation border condition: reaction of two particles proceeds with finite rate;
- Neutral *x* charged particles
- Mutual effects of particles and their influence on diffusion
- **Competitiveness of reactions governed by diffusion**

Water radiolysis: reactions of intermediates with admixtures

Principle of competitive kinetics:

-reaction of molecules A, B with OH radicals -

$OH\cdot + A = products$

$OH\cdot + B = products$

$-d[A]/dt = k_A[A][\cdot OH]; -d[B]/dt = k_B[B][\cdot OH]$

(k... rate constant of bimolecular reaction $Lmol^{-1}s^{-1}$*)*

$-d[OH\cdot]/dt = -(d[A]/dt + d[B]/dt)$

Probability of reaction of $OH\cdot$ *with species A or B:*

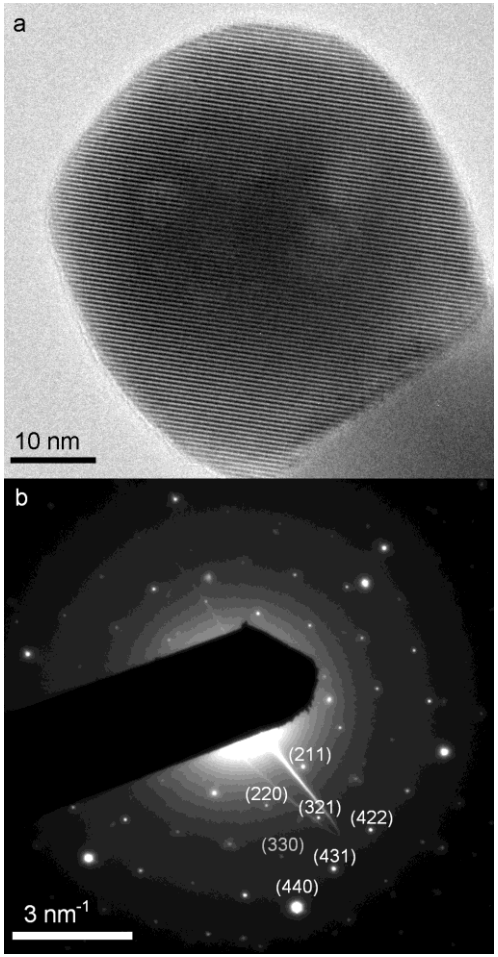
$P_{A+ OH\cdot} = k_A[A]/ (k_A[A]+ k_B[B])$

$P_{B+ OH\cdot} = k_B[B]/ (k_A[A]+ k_B[B])$

RADIATION SYNTHESIS

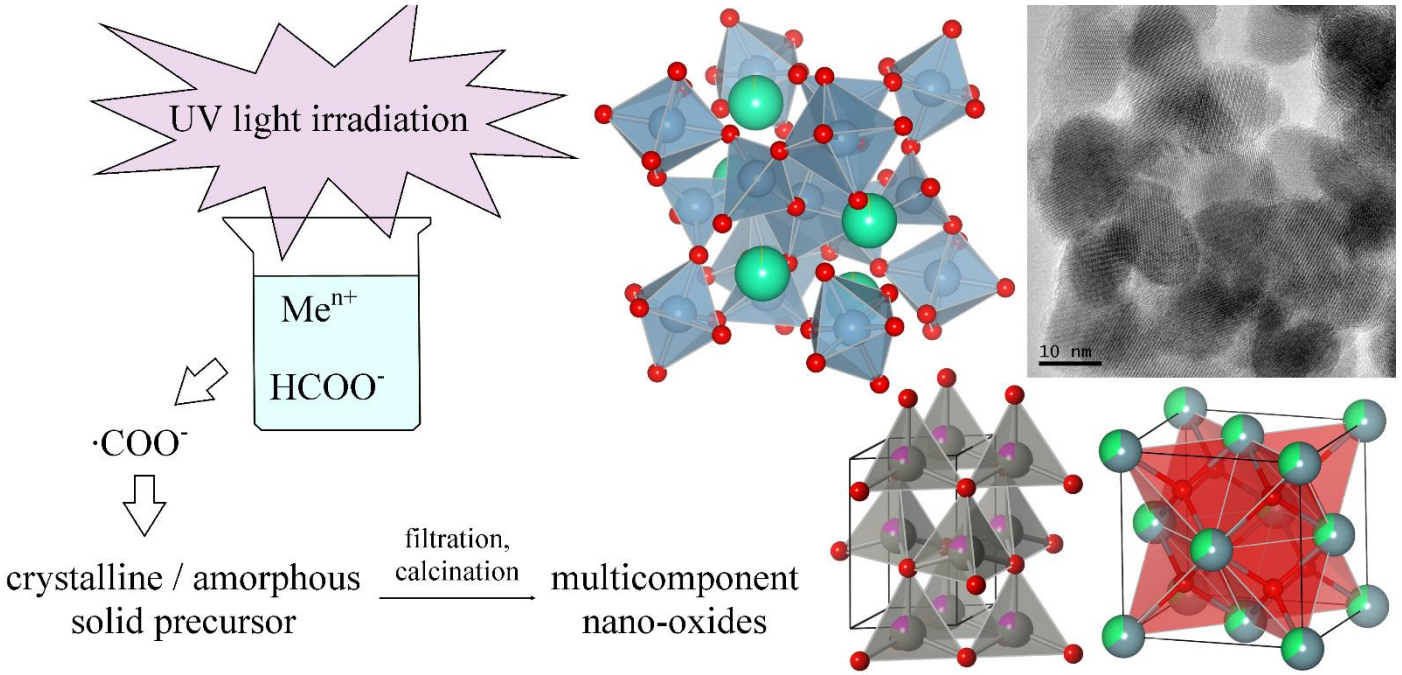
Why radiation method?

- Synthesis is very fast, simple and flexible.
- High yields of nanomaterials. No strict control of experimental conditions (temperature, pH) is required.
- High level of interaction between constituents.
  - Only comparatively mild heat treatment is necessary to obtain oxidic compounds.
- Prepared nanoparticles have narrow size distribution.
- Prepared materials have high chemical and phase purity.



Y_2O_3:Eu. Cuba et al., J. Nanopart. Res. 2012

5 steps of synthetic procedure



1. Irradiation of aqueous solutions containing precursors (i.e. ***soluble metals salts*** and ***radical scavengers***) by IR/UV radiation
2. Reaction of precursors with excited states and/or products of water photo/radiolysis
3. **Formation of finely dispersed solid phase („nano“ scaled, 1-10 nm)**
4. Separation of solid phase
5. Characterization, additional processing

Radiation sources

- Linear electron accelerator LINAC 4-1200 (Tesla v.t. Mikroel)
  - Electron energy 4.5 MeV
  - Alanine dosimetry

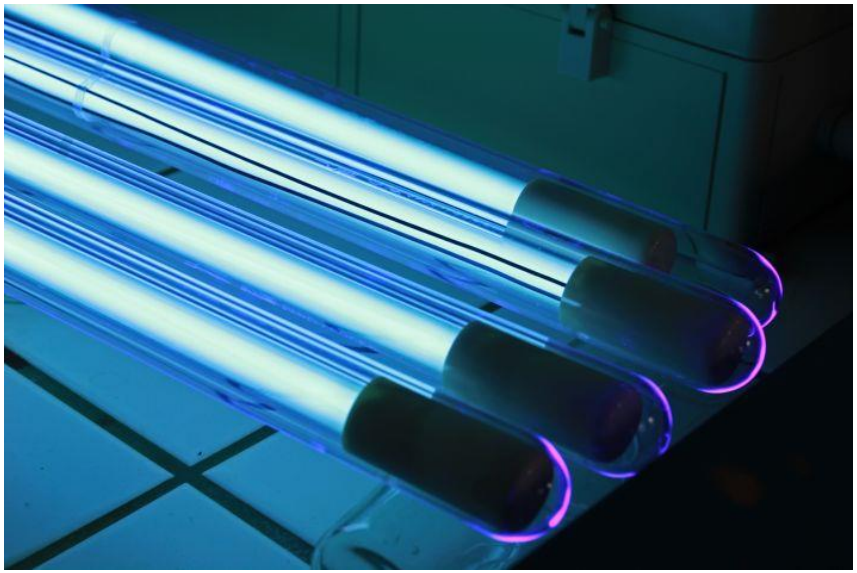
- Gamma ^{60}Co RN sources Gammacell 220
  - Dose rates 35 Gy/h – 5 kGy/h
  - Fricke dosimetry

➧ ***Doses tens of kGy***

Radiation sources

- The medium and low pressure mercury UV lamps
  - ➢ Wavelengths of emitted photons 200-580 nm
  - ➢ The ferrioxalate and iodide/iodate actinometry

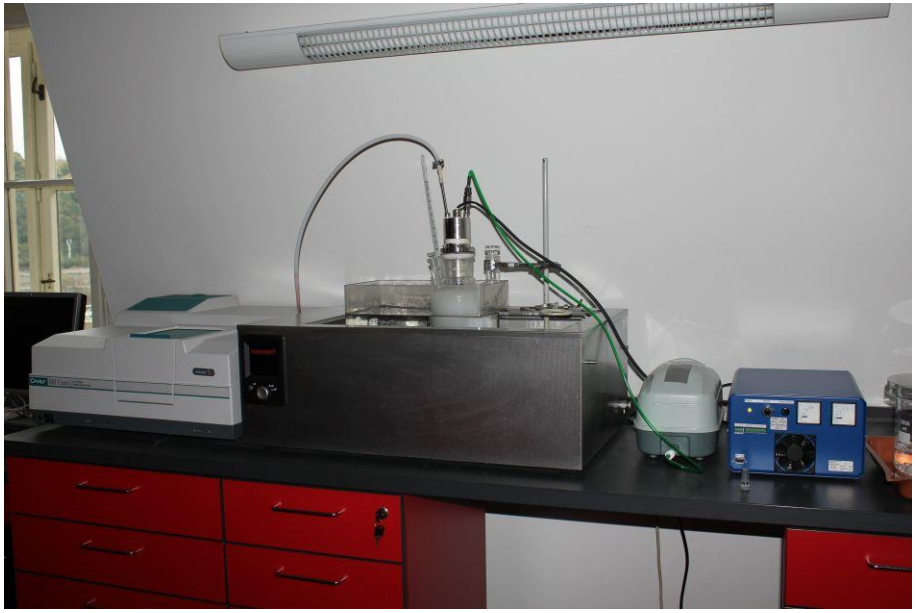
- Nd:YAG solid state laser
  - ➢ Wavelength of emitted photons 266 nm
  - ➢ Pulse length 2.5 ns; rep. frequency 10 Hz
  - ➧ ***Irradiation takes tens of minutes***



Solutions for irradiation

- Nanoparticles prepared via IR/UV irradiation of aqueous solutions containing
  - soluble metal salts
  - radical scavenger / reducing agent

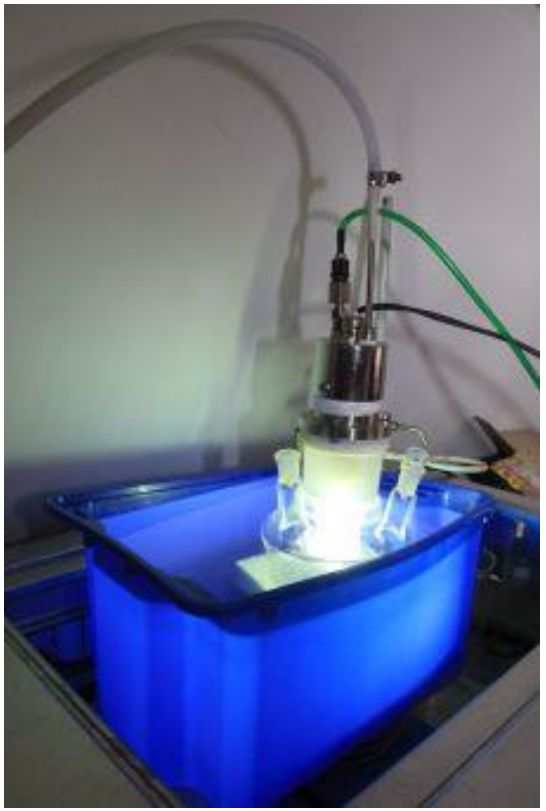
- Molar concentration of all compounds in the range 10^{-3}-10^{-2} mol x dm^{-3}



Photoreactor with UV/Vis spectrophotometer

Separation and processing of solid phase

- Separation via microfiltration
- Drying at laboratory temperature
- Heating in vacuum, air or inert atmosphere
- Further processing - press-compacting



Characterization of irradiated solutions and solid phase

- Speciation calculations
- UV-VIS spectrophotometry
- Measurement of pH

- X-ray fluorescence (**XRF**)
- Radioluminescence measurement (**RL**)

- Thermal analysis
- X-ray powder diffraction (**XRPD**)
- Specific surface area measurement (**SSA**)
- Electron microscopy (**SEM**, **HRTEM**, **SAED**)

OH radical scavenging, formation of reductive species

$$HCOO^- + \dot{O}H / \dot{H} \rightarrow \dot{C}OO^- + H_2O / H_2$$

Buxton et al. 1988

$$(CH_3)_2CHOH + \dot{O}H / \dot{H} \rightarrow (CH_3)_2\dot{C}OH + \dot{C}H_2CHOHCH_3 + H_2O / H_2$$

$$(CH_3)_2C=O \xrightarrow{270\,nm} {}^1[(CH_3)_2C=O] \xrightarrow{inter-system\ crossing} {}^3[(CH_3)_2C=O]$$

Calvert and Pitts 1966

$$[(CH_3)_2C=O] + (CH_3)_2CHOH \rightarrow 2(CH_3)_2\dot{C}OH$$

Direct formation of metallic/oxide nanoclusters

$$M^{n+} + e^-_{aq} \rightarrow M^{(n-1)+}$$

Remita and Remita 2010

$$M^{+1} + H\cdot \rightarrow M^0 + H^+$$

$$M^{n+} + \dot{C}OO^- \rightarrow \left[M^{n+}COO\right]^{(n-1)+} \rightarrow M^{(n-1)+} + CO_2$$

Neta et al. 1996

$$M^{n+} + (CH_3)_2\dot{C}OH \rightarrow \left[M(CH_3)_2COH\right]^{n+} \rightarrow M^{(n-1)+} + (CH_3)_2C=O + H^+$$

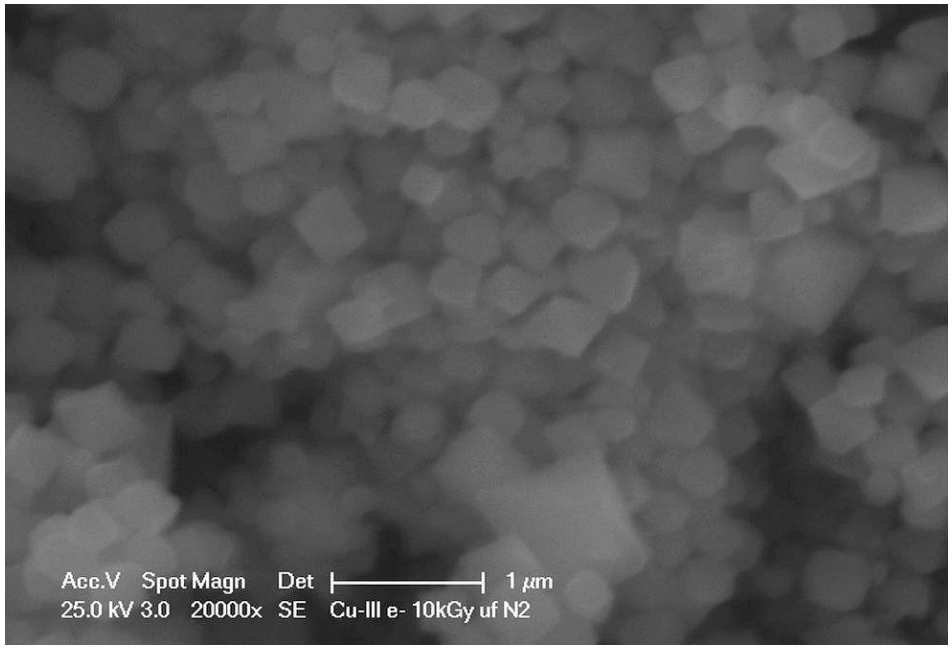
$$2\,M^{(n-1)+} \rightarrow M^{n+} + M^{(n-2)+}$$

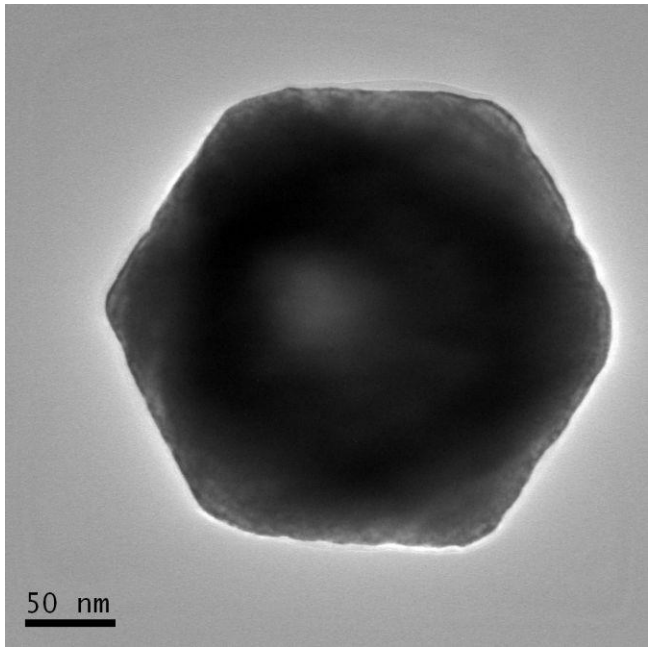
Barta et al. 2010

$$2\,M^+ + 2\,OH^- \rightarrow 2\left[MOH\right] \rightarrow M_2O + H_2O$$

Directly formed - cuprous oxide

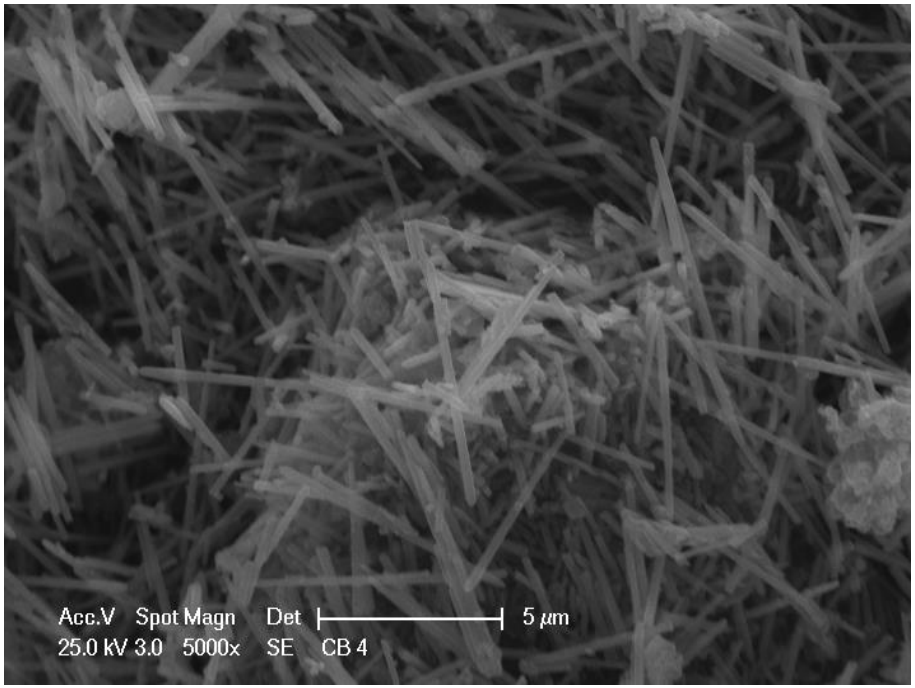
$Cu^{2+} + CO_2^- \rightarrow Cu^+ + CO_2$
$Cu^+ + CO_2^- \rightarrow CuCO_2$
$CuCO_2 + Cu^{2+} \rightarrow 2Cu^+ + CO_2$
$CuCO_2 + Cu^+ \rightarrow Cu_2^+ + CO_2$
$2Cu^+ + 2OH^- \rightarrow 2Cu(OH) \rightarrow Cu_2O + H_2O$

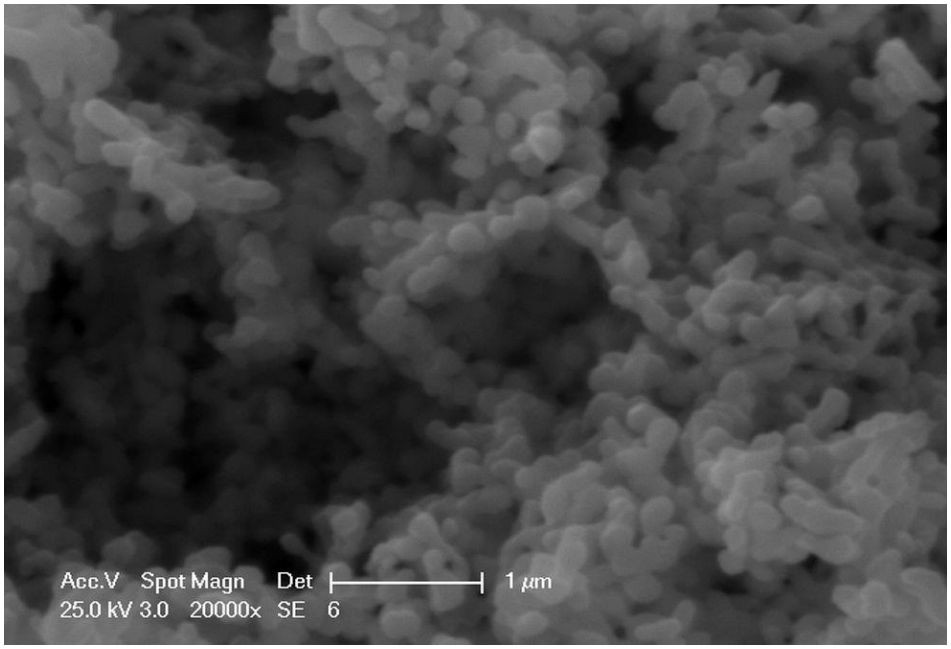




Barta et al., J. Radioanal. Nucl. Chem. (2010).

Directly formed - zinc oxide





Zinc oxide prepared by gamma irradiation from solutions containing sufractant (CTAB)

Nanoparticles of zinc oxide increase with heat treatment; at 600°C, they grow to cca 80 nm

Cuba et al., Radiat. Phys. Chem. 2010

Indirect formation

- Radiation induced precipitation of amorphous/weakly crystalline solid phase
  - Carbonates, hydroxides, etc.
- Followed by calcination
  - Different atmospheres affect the type of resulting materials
  - Temperature of calcination affects particle size, crystallinity, specific surface area, porosity, etc.

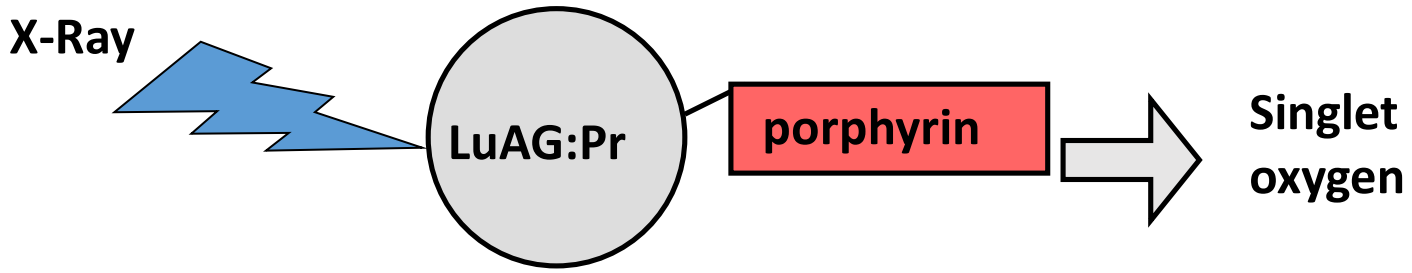
Indirectly formed - scintillating nanooxides

- These nanomaterials:
  - Often contain at least two „components“ (e.g. metal ions, oxide structures, crystalline phases).
  - High level of interaction between those components occurs (i.e. **not** a mechanical mixture)
  - Low concentration of other doping ions might be introduced
  - Nanosized grains - dimensions less than 100 nm

Prospective applications of scintillating nanomaterials

- Highly efficient nanoscintillators
- Band-gap engineered nanophosphors
- Cores of drugs for x-ray induced photodynamic therapy (**PDTX**)
- Precursors for the manufacture of optical ceramics or composite materials

PDTX principle



- Drug introduced into patient.
- It accumulates in a tumour via EPR effect.
- X-Ray irradiation is absorbed by „core“ nanoscintillator, subsequently emitted UV is absorbed by porphyrin.
- Singlet oxygen is generated, killing tumour cells.

Doped synthetic garnets as nanoscintillators

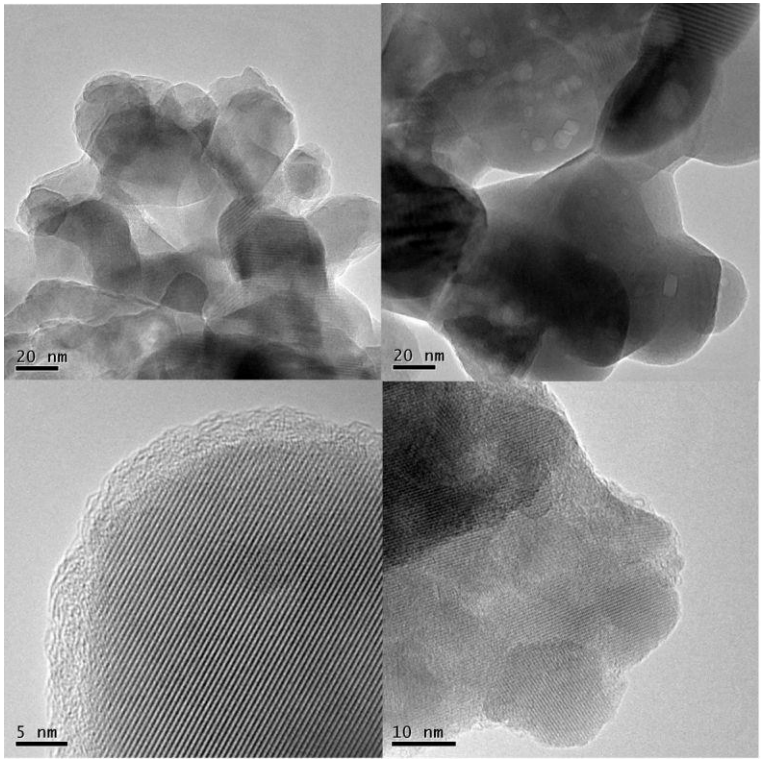
- Irradiated solutions containing:
  - Nitrates/chlorides of all metals (Y, Lu, Al, Ce, Eu, Pr) in stiochiometric ratios (~ 10^{-3} mol x dm^{-3})
  - Ammonium/Potassium formate (~ 10^{-2} mol x dm^{-3})
- Solid precursors fomed are amorhous
- Pure garnet phase typically formed at temperatures above 800°C (**particle size ~ 30 nm**)
- Optimum luminescence typically obtained at 1200°C (**particle size ~ 50 nm**)

Barta et al., J. Mater. Chem. 2013

Yttritum-aluminium garnet ($Y_3Al_5O_{12}$; YAG)

- Aluminium chloride, yttrium nitrate, ammonium/potassium formate
  - *Doped with cerium nitrate*

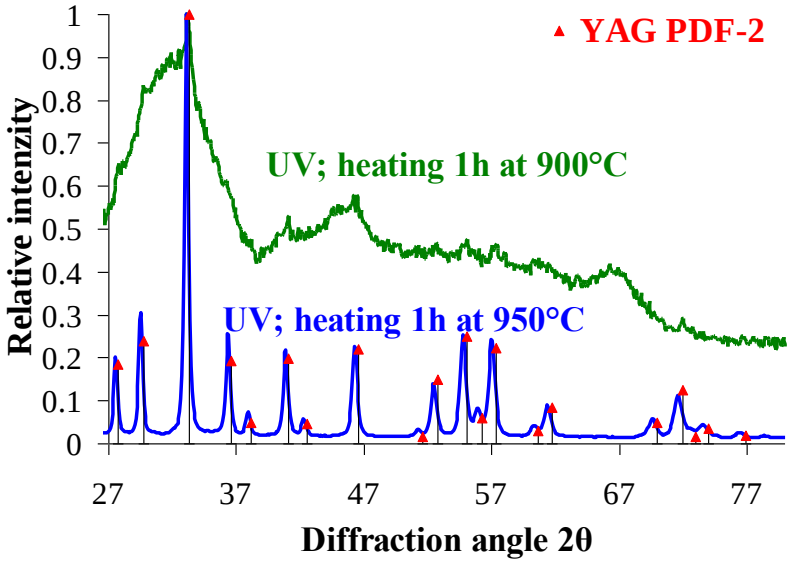
- ***UV irradiaton*** – regardless of temperature of heat treatment, only pure YAG phase detected
- ***Accelerated electrons*** – results are remarkably similar to those obtained under UV radiation

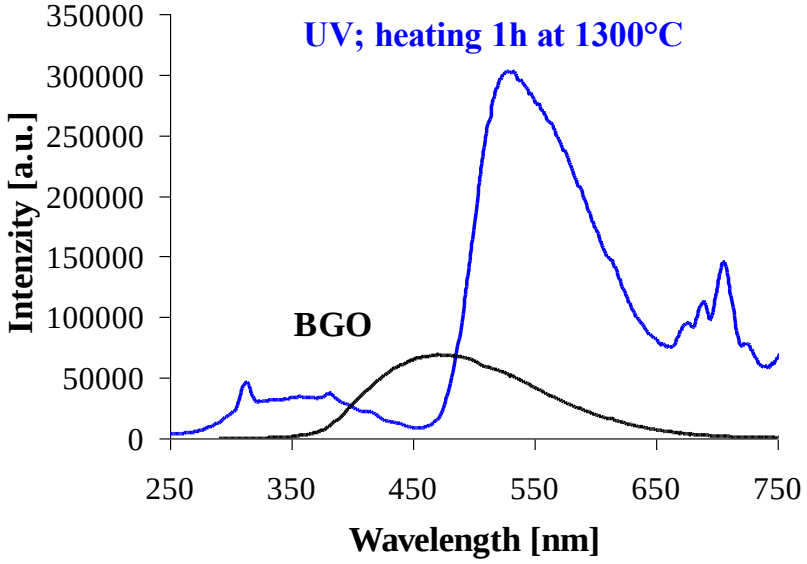


HRTEM image of YAG prepared via UV (***L***) and e^- (***R***)

YAG – XRD and RL results

- UV irradiation leads to formation of pure YAG (or YAG:Ce) with intensive RL
- RL intensity preserved even after ceramization of YAG nanopowder



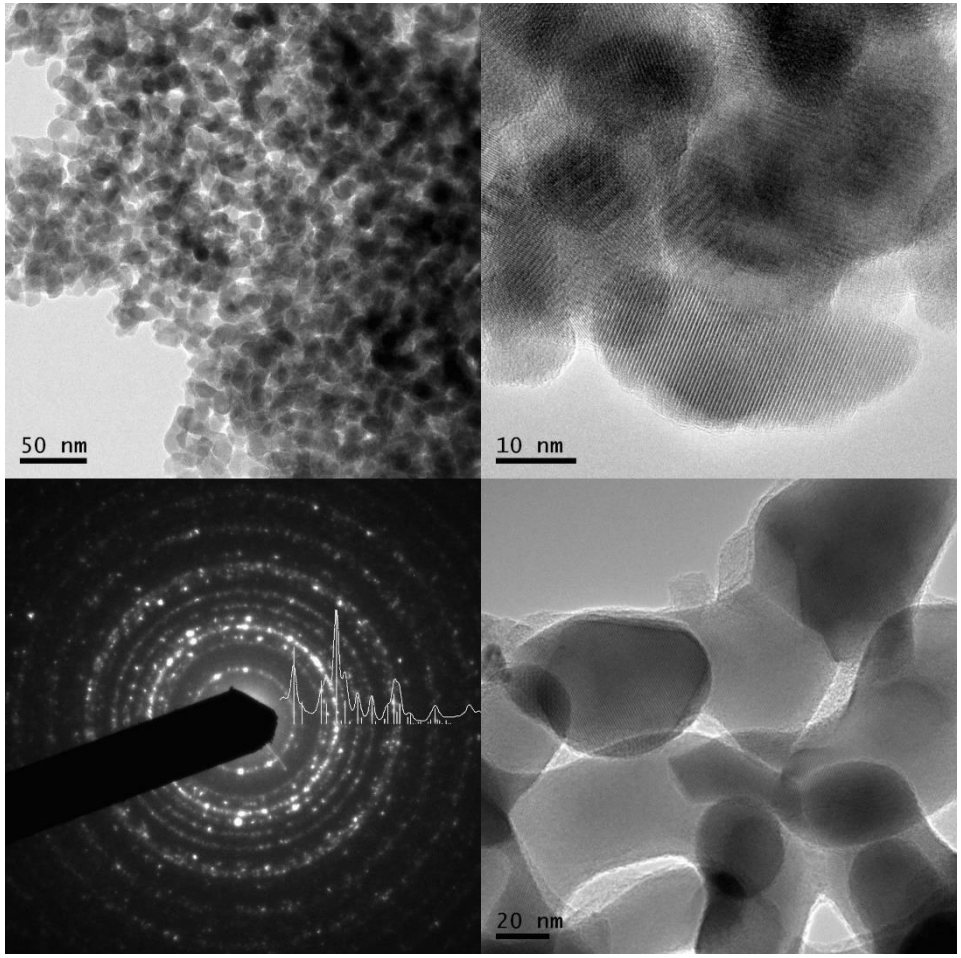


Cuba et al., Radiat. Phys. Chem. (2011).

Lutetium-aluminium garnet ($Lu_3Al_5O_{12}$ LuAG)

- Lutetium and aluminium nitrates, ammonium/potassium formate

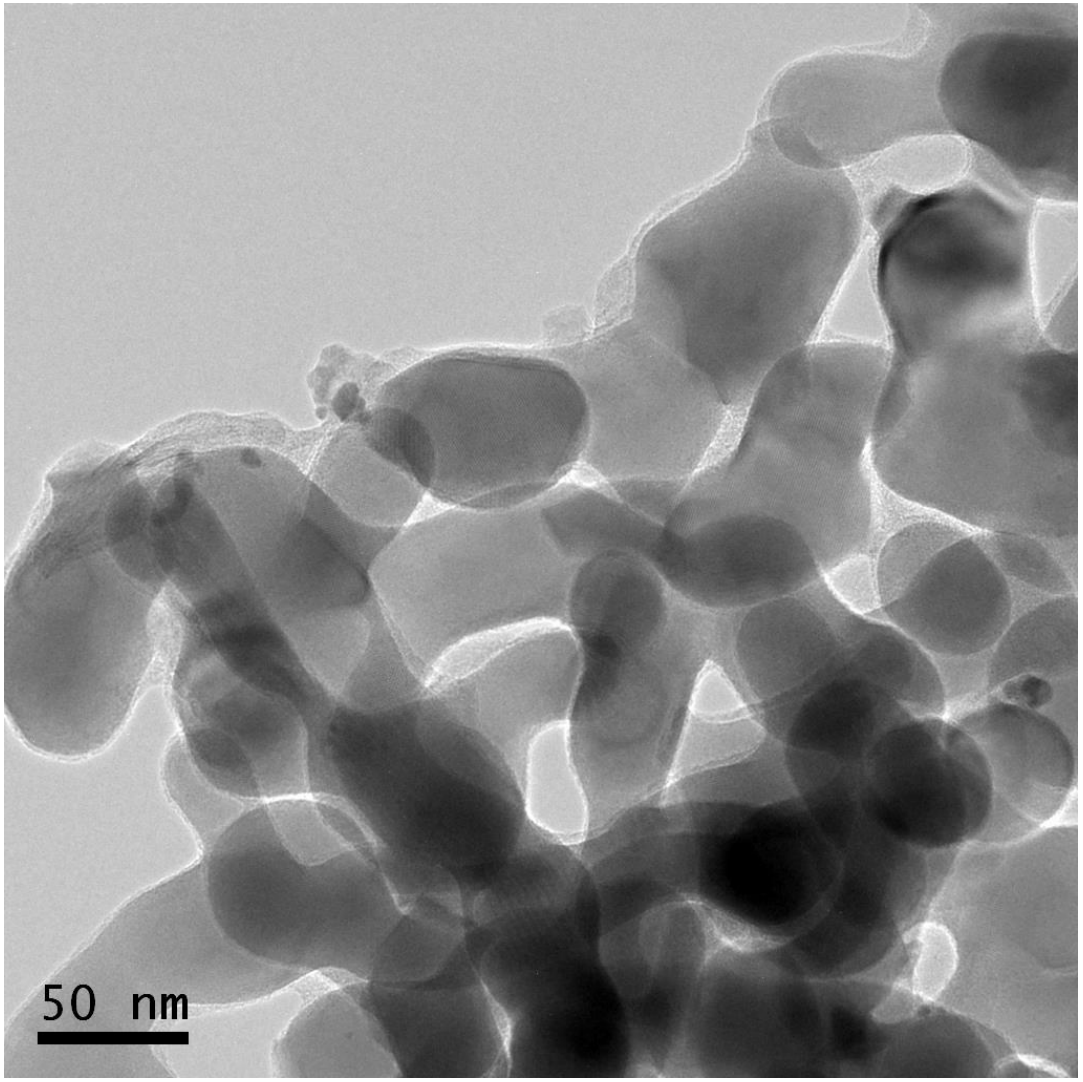
- Similarly to YAG preparation, irradiation leads to the formation of pure LuAG phase



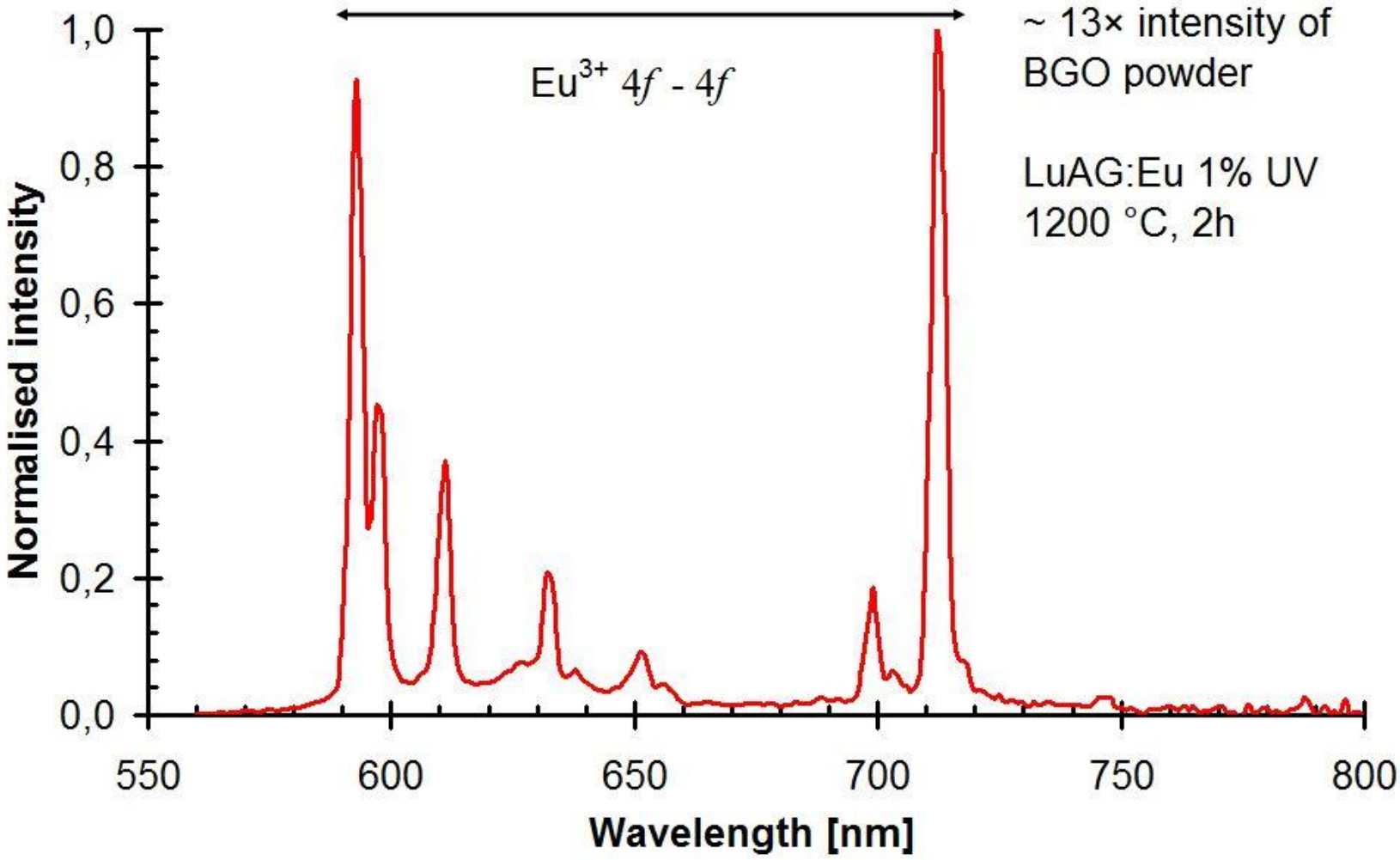
Barta et al., J. Mater. Chem. (2012).

HRTEM of LuAG optimized for high scintillation efficiency

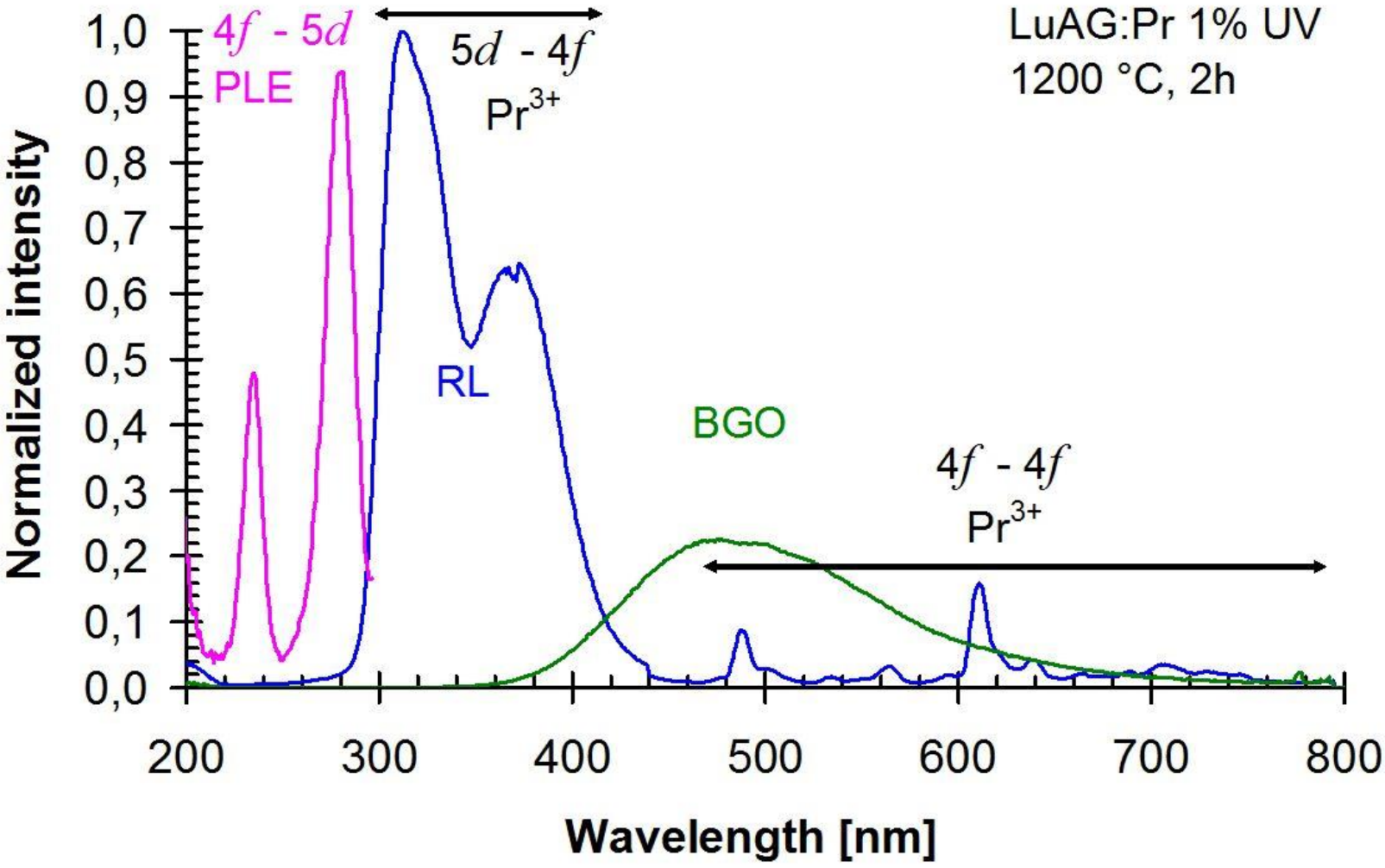
- Doped with Eu/Pr
- 1200°C
- 2h
- Air



LuAG:Eu RL


Eu3+ 4f - 4f
~ 13× intensity of BGO powder
LuAG:Eu 1% UV
1200 °C, 2h
Normalised intensity
1,0
0,8
0,6
0,4
0,2
0,0
550
600
650
700
750
800
Wavelength [nm]

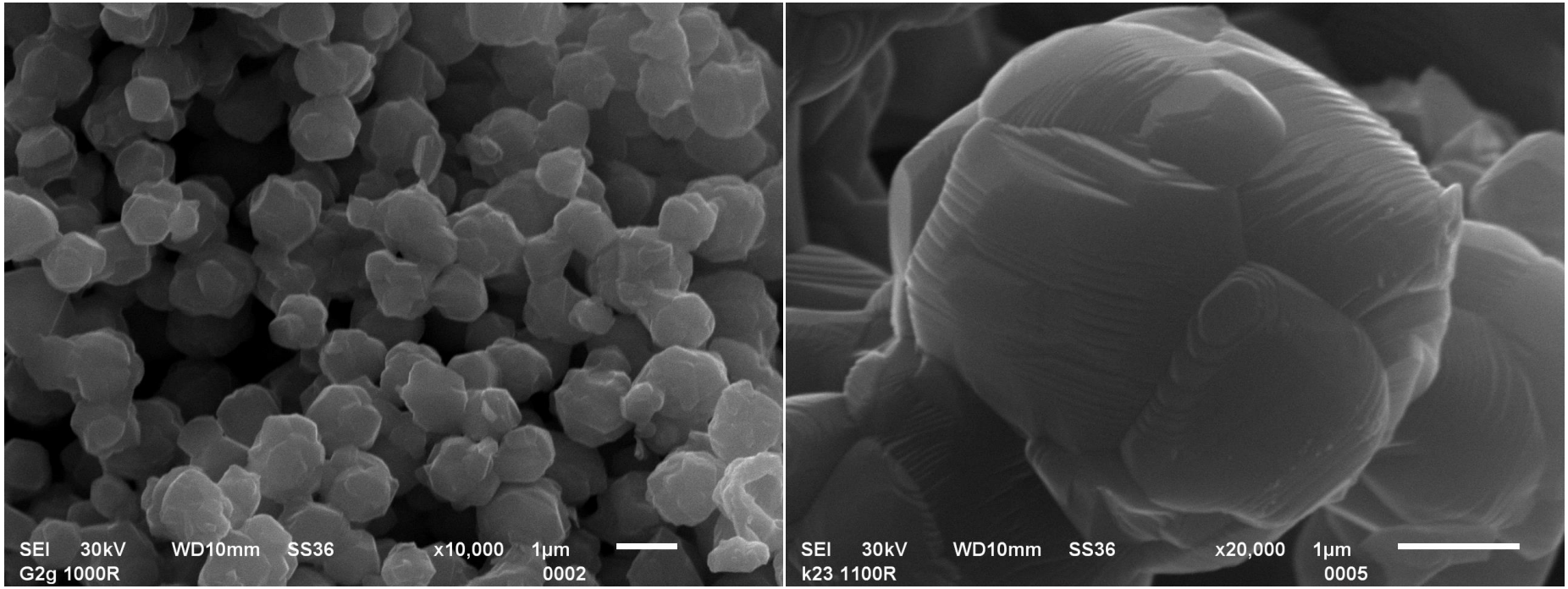
LuAG:Pr RL


LuAG:Pr 1% UV
1200 °C, 2h
4f - 5d
PLE
5d - 4f
Pr3+
RL
BGO
4f - 4f
Pr3+
Normalized intensity
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
200
300
400
500
600
700
800
Wavelength [nm]

ZnCd(Mg)O:Ga band gap engineered materials

- Irradiated solutions contained:
  - ✓zinc nitrate, cadmium/magnesium nitrate, gallium nitrate, ammonium formate.
  - ✓hydrogen peroxide
- Crystalline solid precursor formed
- Annealed at 210°C, particle size 10-15 nm.
- Maximum content of Cd/Mg ~ 20%.

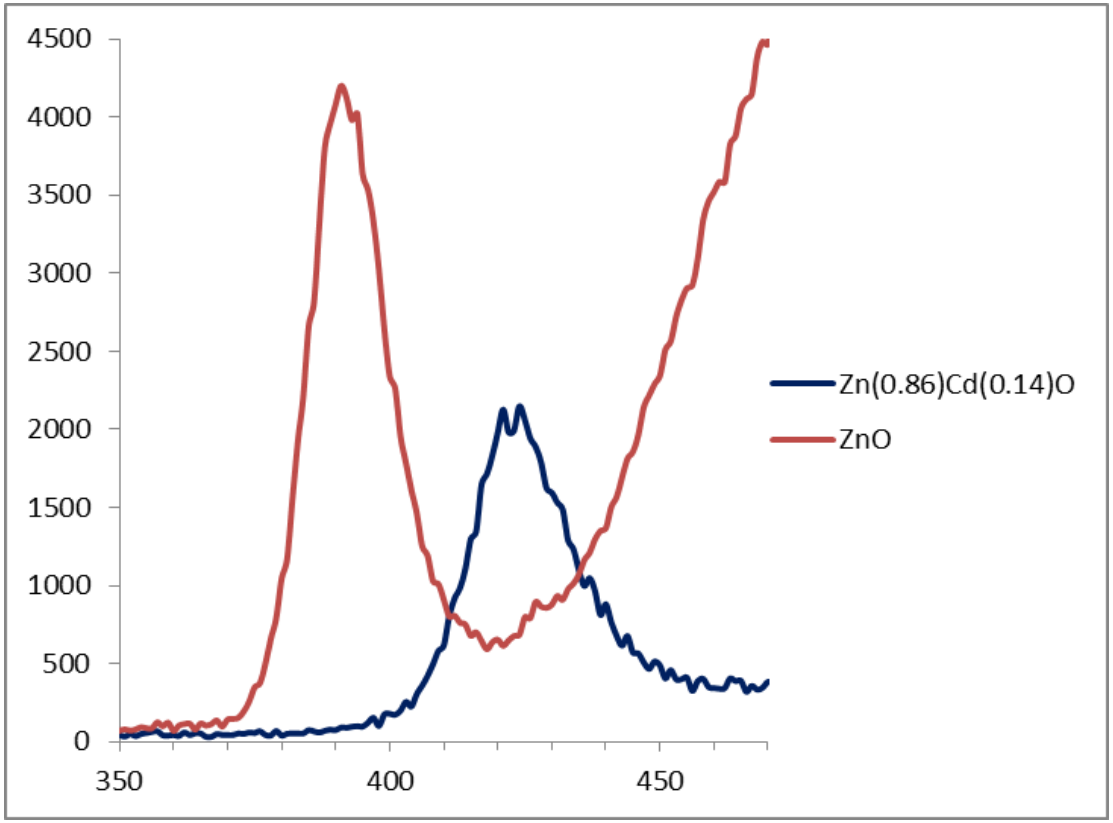
ZnCd(Mg)O:Ga band gap engineered materials



From **nano**- to **micro**- : calcination at 1100°C for optimizing the luminescence

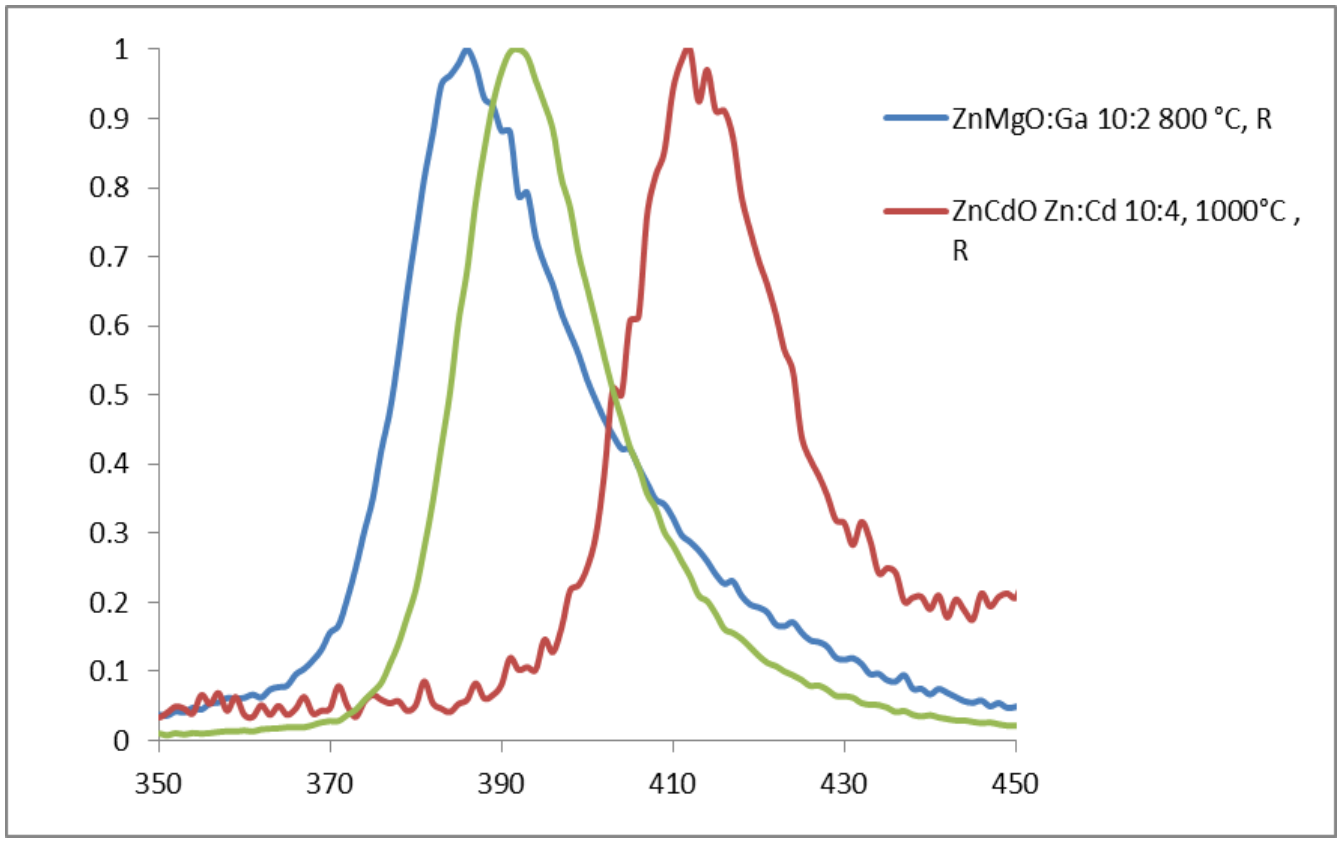
Gbur et al., J. Nanopart. Res. 2011

ZnCd(Mg)O:Ga band gap engineered materials



Radioluminescence Detail of excitonic luminescence for pure ZnO and $Zn_{0.86}Cd_{0.14}O$. Red shift to 425 nm.

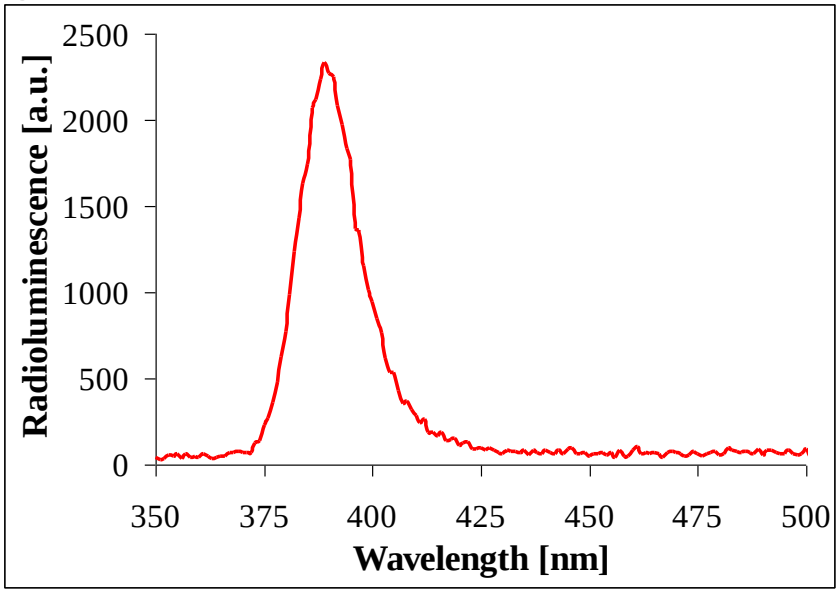
ZnCd(Mg)O:Ga band gap engineered materials



Radioluminescence. Red shift to 412 nm in the case of ZnCdO with ratio Zn:Cd = 10:4 and blue shift to 385 nm in the case of ZnMgO:Ga with ratio Zn:Mg = 10: 2

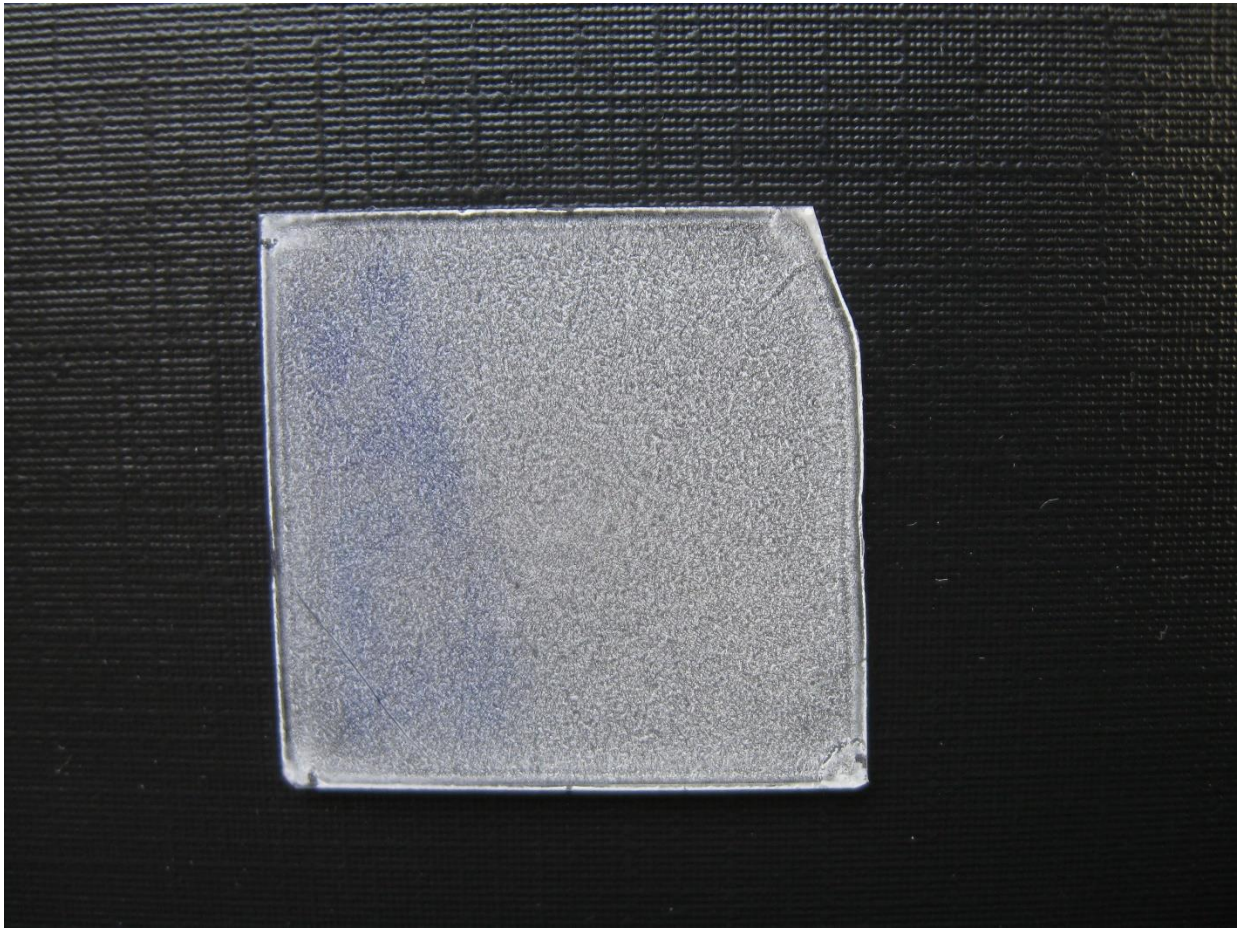
ZnO:Ga - based nanocomposites

- ZnO nanocrystalline powder is difficult to proces
- For possible applications, either optical ceramics or Composite materials need to be developed
- ZnO:Ga(La) embedded into transparent matrix of polyurethane dimethacrylate
- Matrix assembled from mono- and bis-urethane monomers via UV-induced polymerization.



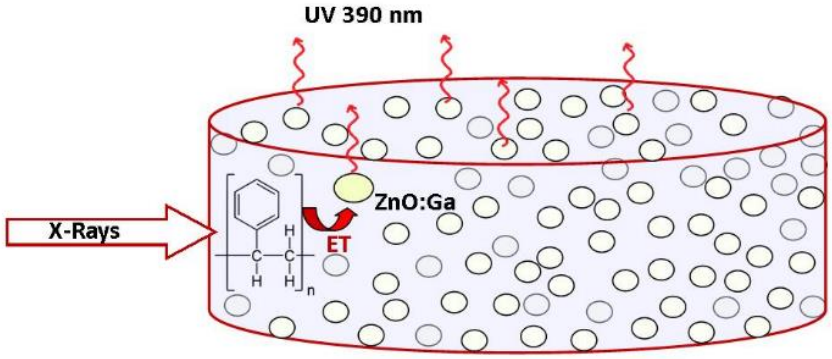
ZnO:Ga - based nanocomposites

- ZnO:Ga powder embedded into the SiO_2 matrix on the glass substrate.
- The starting sol was prepared by mixing the nanocrystalline ZnO with pre-hydrolyzed tetraethylorthosilicate (TEOS).

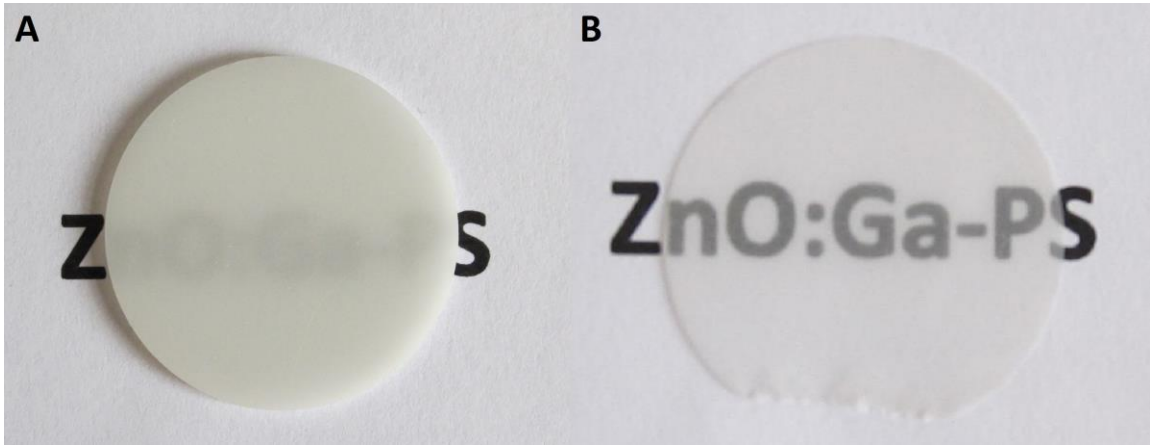


- The initial sol prepared by mixing the nanocrystalline ZnO with pre-hydrolyzed tetraethylorthosilicate (TEOS).
- Formed sol spin-coated on planar optical substrates forming thin films
- The thickness of prepared films is about 600 nm.

ZnO:Ga - based nanocomposites



ZnO:Ga scintillating particles embedded in scintillating polystyrene matrix.
Non radiative energy transfer between the PS matrix and ZnO:Ga
Low transparency of thick samples



Burešová et al. Opt. Express 2016

Conclusions

- Radiation syntheses present simple and fast methods for preparation of various scintillating materials with high chemical purity and narrow particle size distribution
- Method enables easy doping of host material with foreign ions
- In multi-component systems, high level of interaction between components occurs
- Radiation synthesis is thus very convenient alternative for preparation of multicomponent nanoscintillators.
- To obtain crystalline material, usually comparatively low temperature of calcination is required.
- Quality of prepared crystals is demonstrated by very intense radioluminescence.
- Formation and shift of excitonic luminescence has been observed in band gap engineered ZnO based materials, depending on their type and composition.