R&D trends in oxide-based single crystal materials

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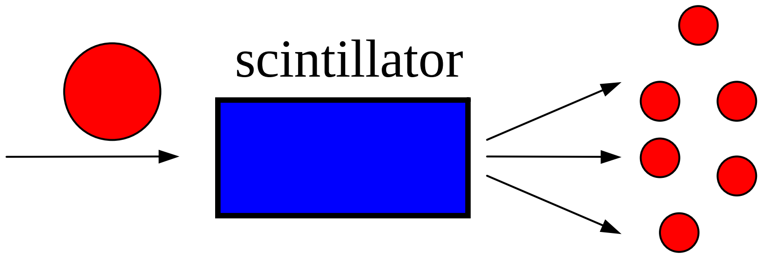
Principle of a scintillator

Spectral and energy transformer

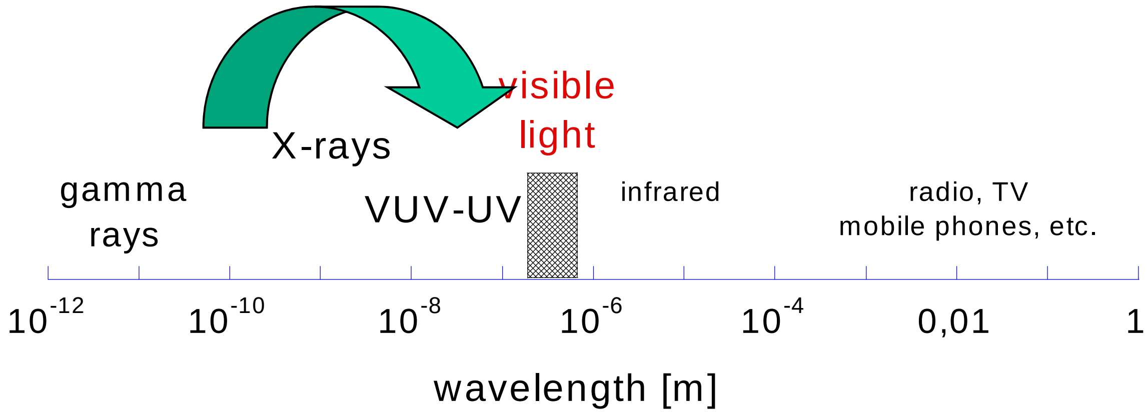


1 photon
(keV - GeV)

n photons
(2 - 4 eV)

Counting of HE photons!

Fast response needed !

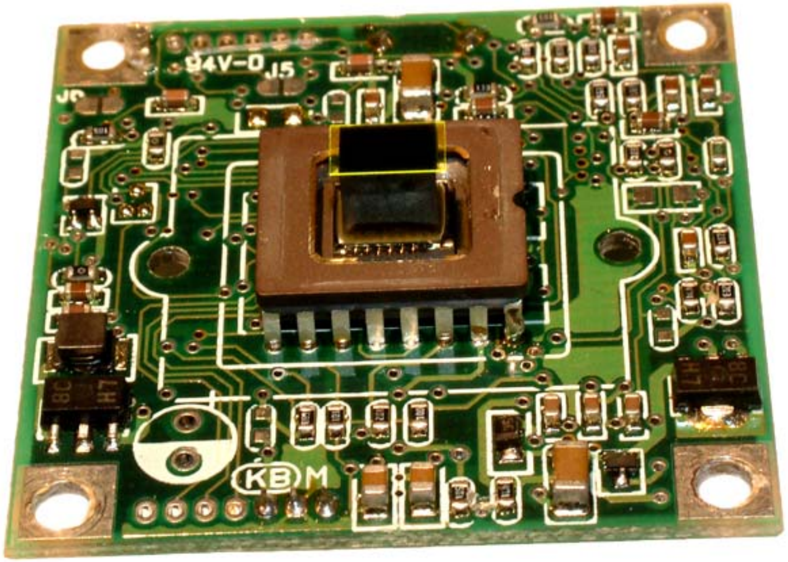


Why we need them – there are no direct sensitive detectors for photons with energy above a few keV

Scintillation detector = scintillator+photodetector

⇒ registration of X-rays or γ-radiation, energetic particles or ions.

Scintillator TRANSFORMS high-energy photons into photons in UV/VIS spectral region, which one can easy and with high sensitivity register by the conventional detectors.



PD, APD, CMOS, CCD …
Si, GaAs, GaN, AlN, InGaN, SiC, diamond

W.C. Roentgen, Science 3, 227 (1896)

*ON A NEW KIND OF RAYS.**

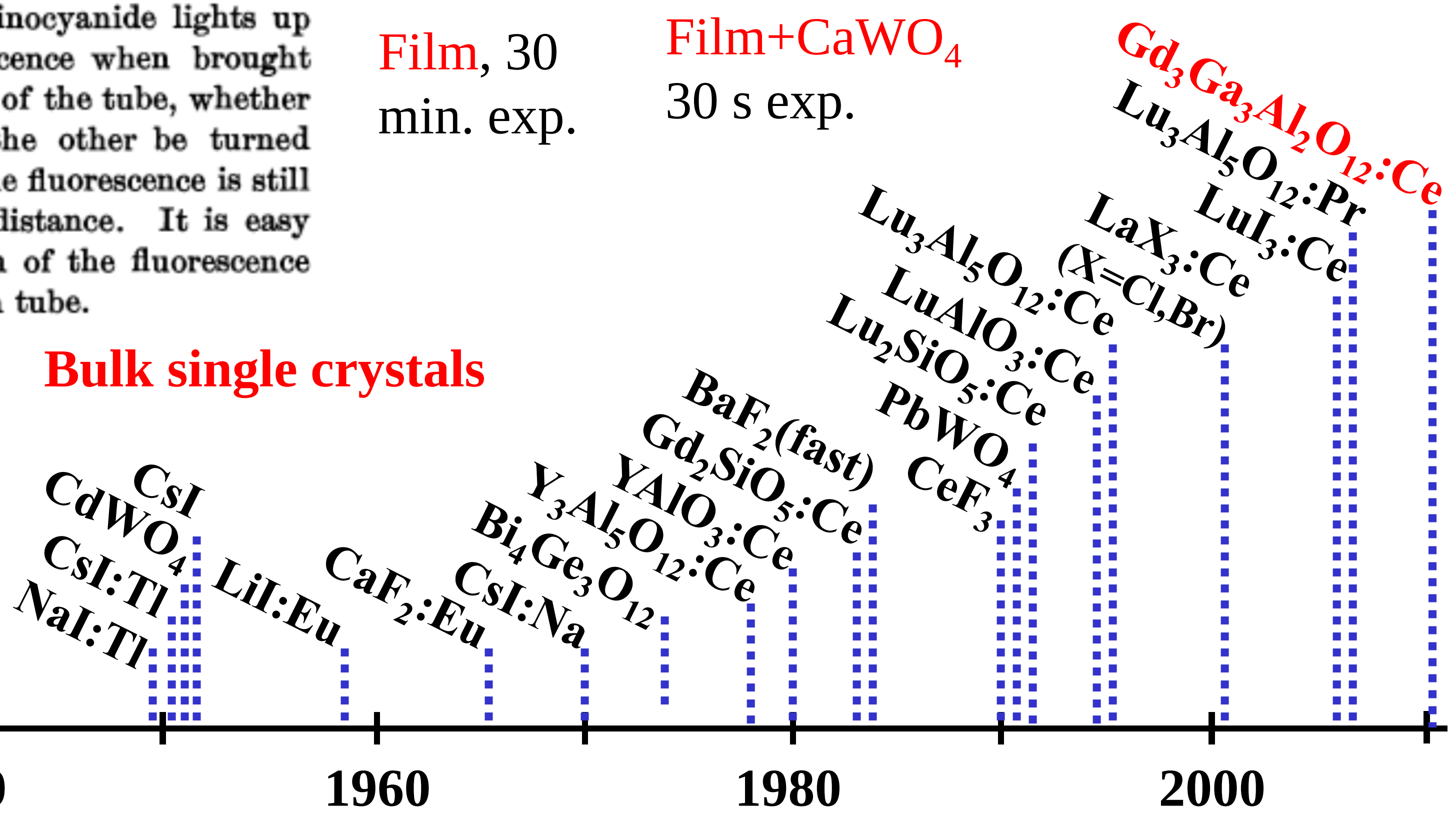
1. A DISCHARGE from a large induction coil is passed through a Hittorf's vacuum tube, or through a well-exhausted Crookes' or Lenard's tube. The tube is surrounded by a fairly close-fitting shield of black paper; it is then possible to see, in a completely darkened room, that paper covered on one side with barium platinocyanide lights up with brilliant fluorescence when brought into the neighborhood of the tube, whether the painted side or the other be turned towards the tube. The fluorescence is still visible at two metres distance. It is easy to show that the origin of the fluorescence lies within the vacuum tube.

Film, 30 min. exp.

Film+$CaWO_4$
30 s exp.

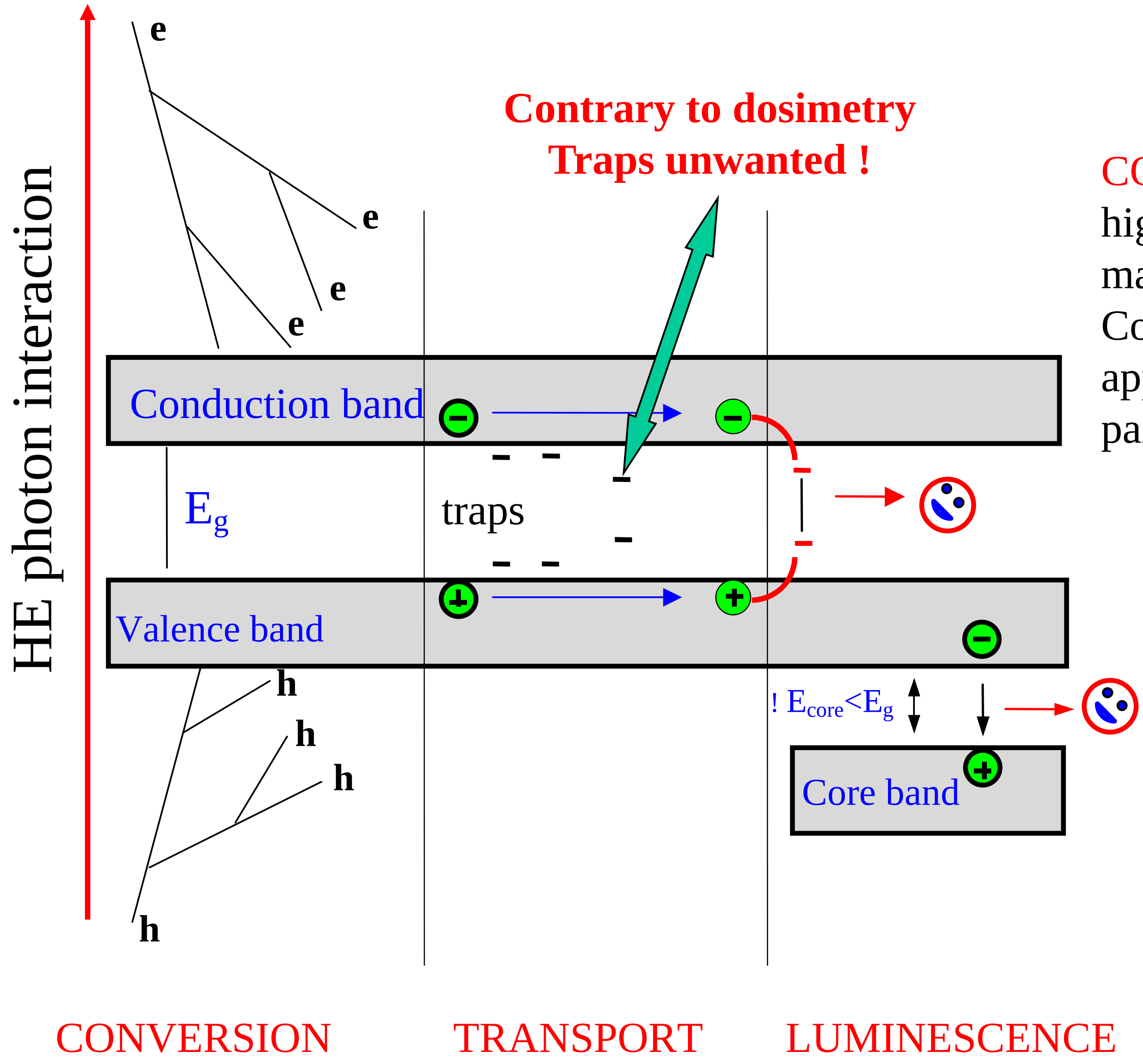
History of scintillators starts short after the discovery of X-rays at the end of 19th century …

$CaWO_4$ powder in 1896



Year of introduction of a scintillation material

Physics of scintillators



CONVERSION -interaction of a high-energy photon with a material through photoeffect, Compton effect, pair production, appearance of electron-hole pairs and their ther-malization

TRANSPORT - diffusion of electron-hole pairs (excitons) through the material, possible (repeated) trapping at defects, nonradiative recombination

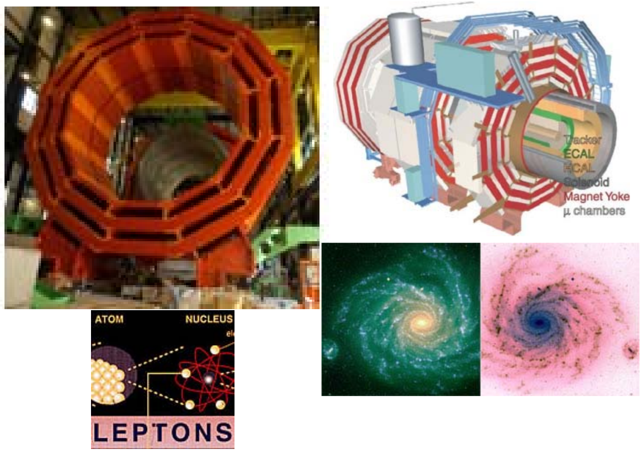
LUMINESCENCE -trapping of charge carriers at the luminescence centre and their radiative recombination

Applications of scintillators

Medical application

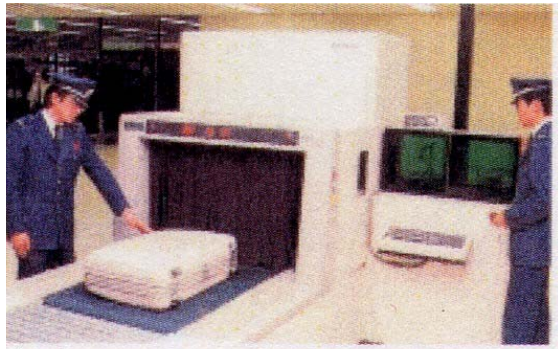
PET, PEM, SPECT, CT

High energy physics



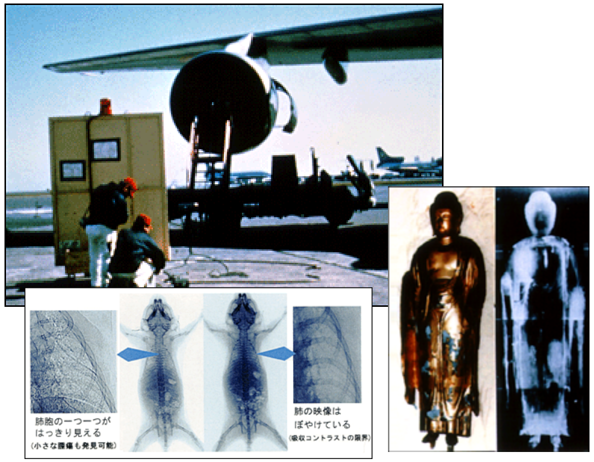
Nuclear, astro- physics, …

Security check



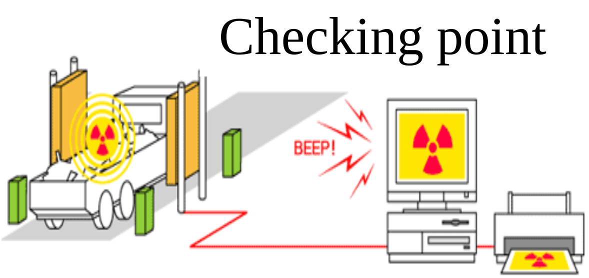
X-ray scanning

Nondestructive analysis



Computed tomography

X&Neutron-based



Homeland security

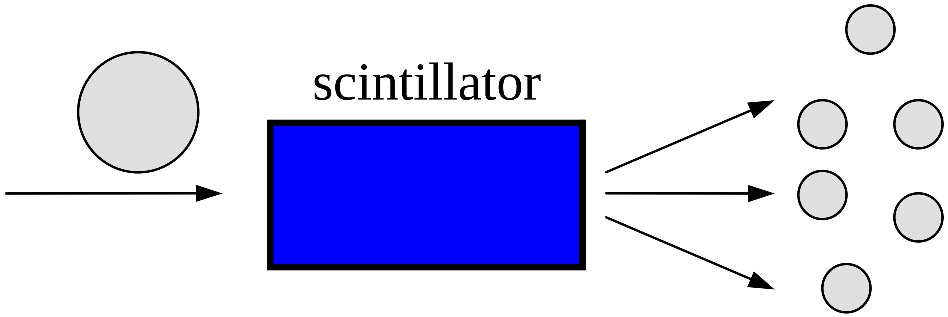
Environmental&other

Radioactive contamination

Parameters and characteristics

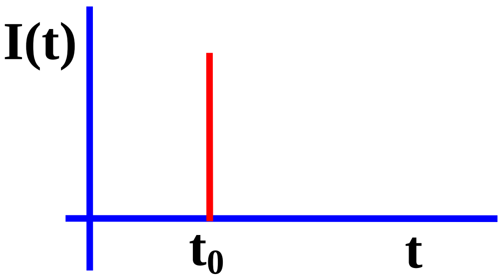
- Integral efficiency and Light yield
- Energy resolution and nonproportionality
- Emission wavelength
- Speed of scintillation response
- Density
- Radiation resistance
- Chemical composition
- Price

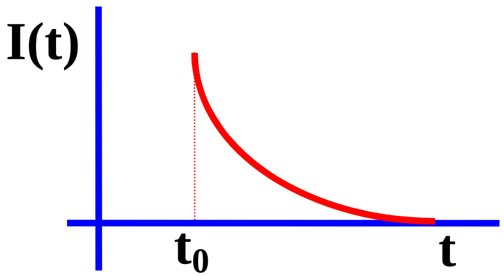
Speed of scintillation response



1 photon
(keV - GeV)

n photons
(1 - 6 eV)





$$I(t) = \Sigma A_i \exp[-t/\tau_i]$$

Duration of the output light pulse is determined by the luminescence decay time of the emission centers, and **timing characteristics of the transport** stage !!!

Strategies in the material engineering

- **Defect engineering (DE)** – targeted codoping (cations) or annealing (anions) to disbalance "natural" defect/trap occurrence and concentration in the material structure
- **Band-gap engineering (BGE)** – more profounded changes in the material electronic band structure due to admixing (alloying) of another chemical component, which is usually possible only in the solid solutions

Defect occurrence is always related to the technological recipe!

Experimental techniques for study of scintillator materials

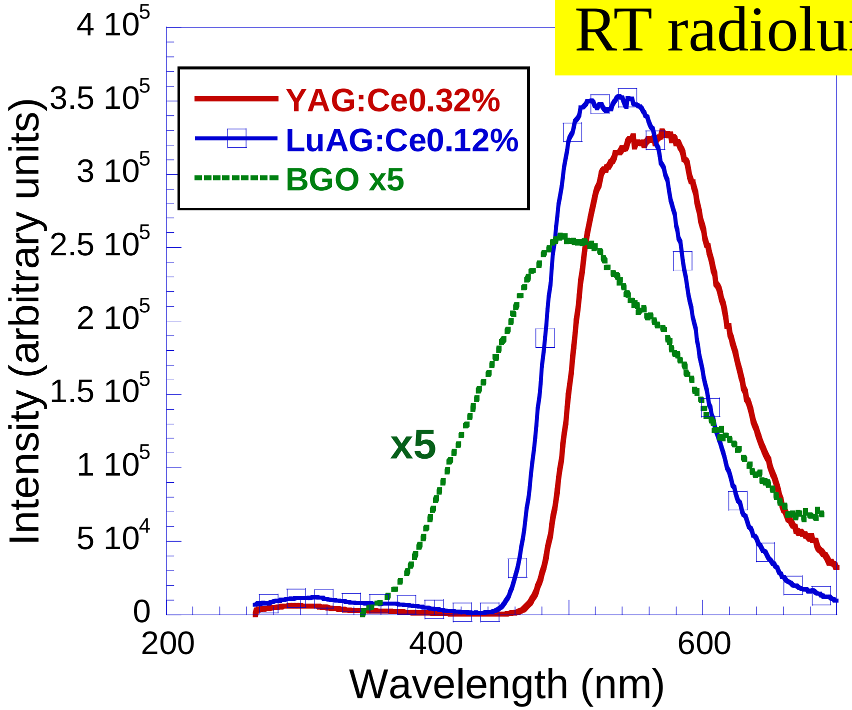
Correlation of several techniques at specifically prepared sample set under well-defined technological conditions:

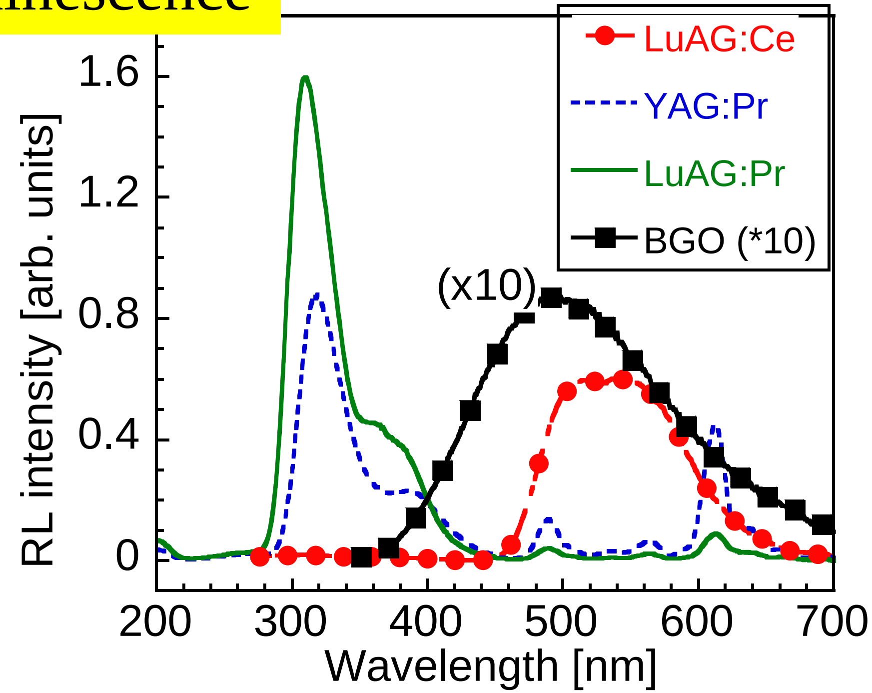
- Thermoluminescence – to visualize trapping states, which take part in the radiative processes, spectra can advise on recombination sites
- Thermally stimulated currents – to visualize complementary nonradiative processes
- Electron paramagnetic (spin) resonance – to understand location and nature of unpaired-spin-containing trapping centers
- Time-resolved emission spectroscopy – to interconnect the luminescence (scintillation) kinetics with the occurrence or non of the defects visualized by the above techniques

These techniques are correlated with the evaluation of practical scintillator characteristics mentioned before ….

BGE strategy -Ce^{3+} and Pr^{3+}-doped $Lu_3Al_5O_{12}$

RT radioluminescence





Light yield (1 μs time gate)

Best YAG:Ce ~ only 3x BGO

Best LuAG:Ce ~ 60% of YAG:Ce

A lot of "slow light" !

The problem:

Retrapping of electrons at shallow traps before their radiative recombination at Ce^{3+} (Pr^{3+}) ions

Nikl, phys. stat.sol. (a) ***201****, R41 (2004)*

Antisite defects in YAG and LuAG single crystals

Ashurov et al, phys. Stat.sol. (a) ***42****, 101 (1977)*

Antisite defect is the most easy defect configuration in AG lattice
their existence is confirmed by both theoretical and experimental results

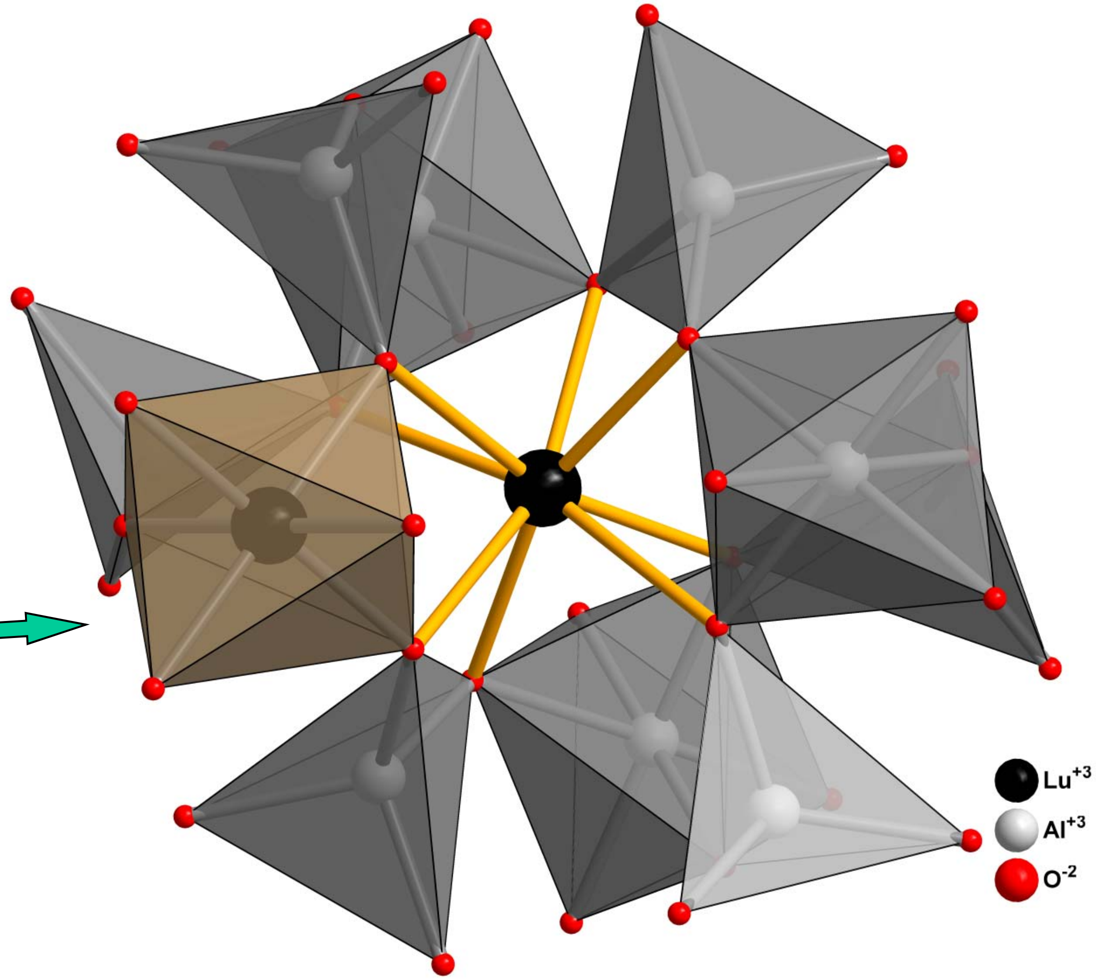
Exchange of Y(Lu) and Al ions is an inevitable consequence of the growth from high temperature melt

We propose:

CB

Electron trap

VB



Defect formation in AG by theoretical calculations

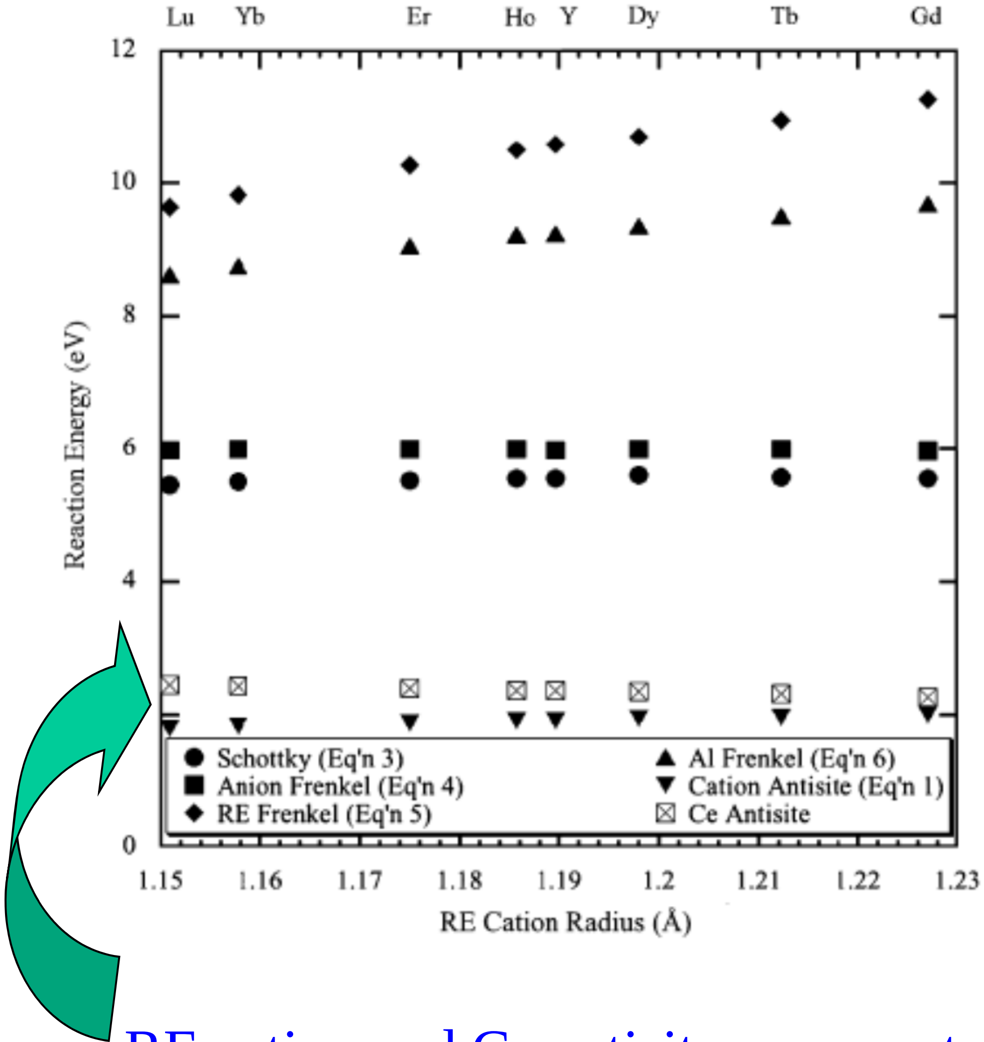
Stanek et al, NIMA 579 ,27 (2007)

Kuklja, JPCM 12, 2953 (2000)

Intrinsic disorder in stoichiometric YAG is dominated by antisites. An antisite substitution $Y_{Al(oct)}$ causes a distortion of the YAG crystalline lattice shortening the Y–O bond length; the calculated value is in excellent agreement with the EXAFS measurements.

We propose:

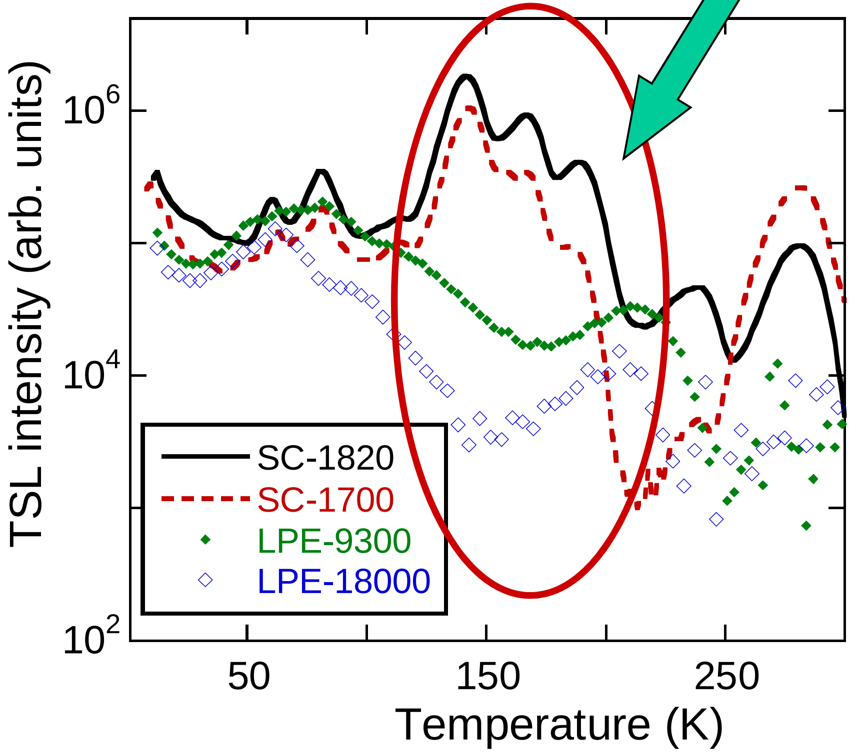
Shortening Y-O bond can lower the energy level of the 4d orbital of Y^{3+} and shallow electron trap is formed!



RE cation and Ce antisites are most easily formed over all the group of Lu-Y-Gd AL garnets!

Shallow electron traps in $Lu_3Al_5O_{12}$:Ce(Pr) revealed in TSL glow curves

It was shown that the shallow electron traps associated with the Lu_{Al} antisite defects are responsible for major part of slow decay components in Cz-grown LuAG:Ce(Pr) single crystals

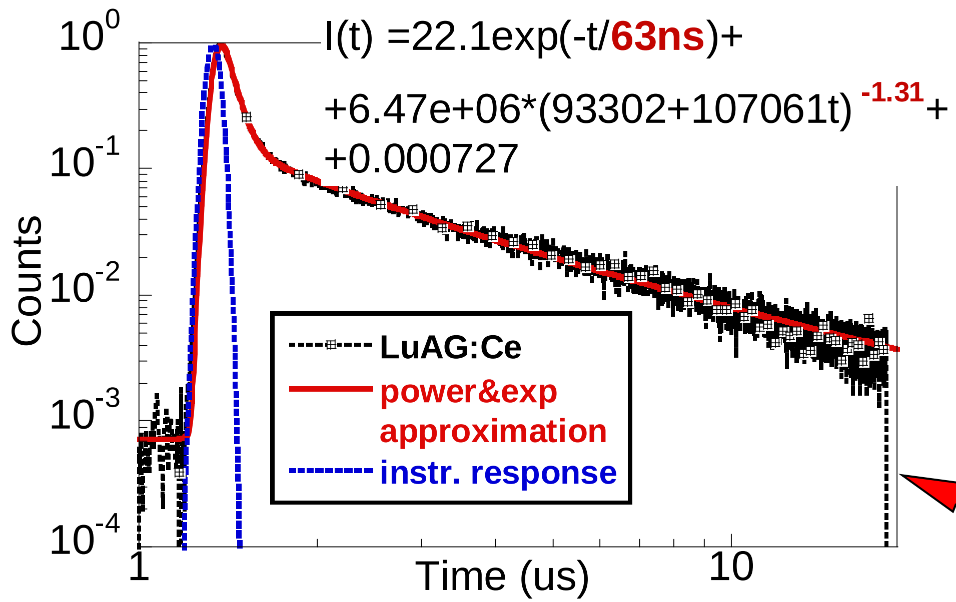


TSL glow curves of the LuAG:Ce single crystals SC-1820, SC-1700 and films LPE-9300 and LPE-18000 samples after X-ray irradiation at 10 K. Similar X-ray irradiation doses were applied to all the samples.

Can we get rid of these electron traps in the bulk melt-grown single crystals???

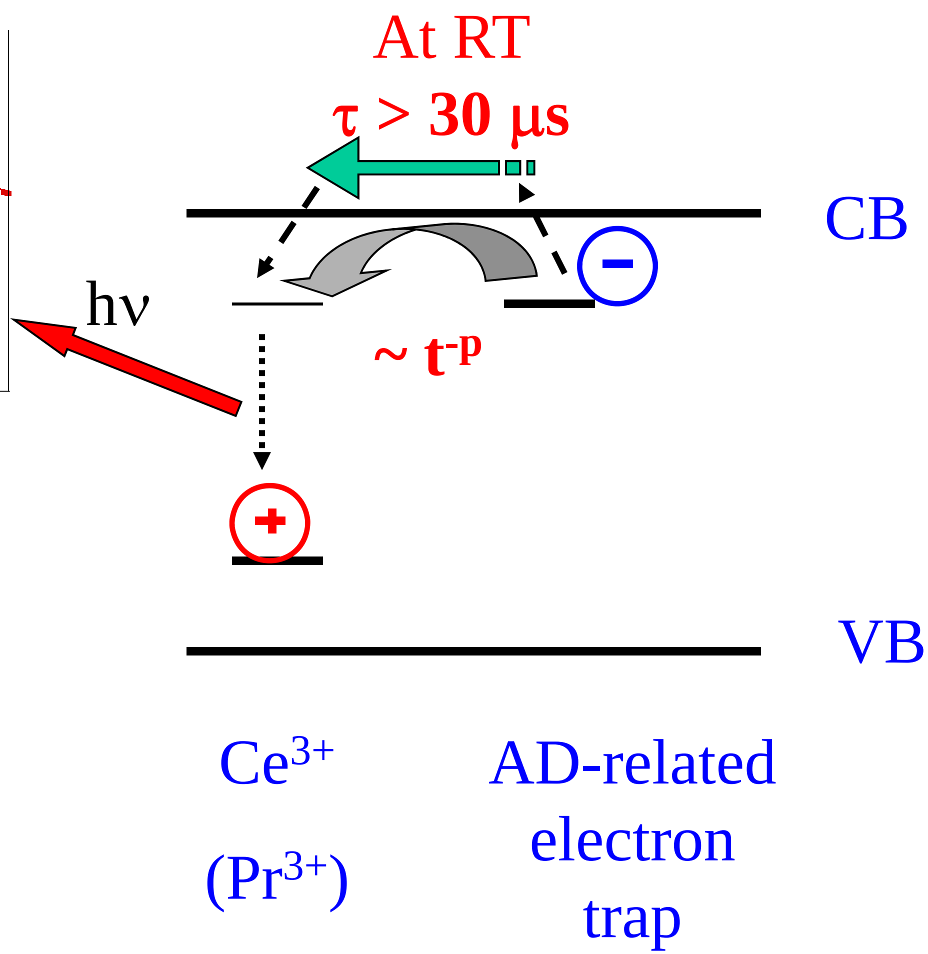
Nikl et al, phys. stat. sol. (b) ***242,*** *R119 (2005)*

Scintillation decay at RT



Data from *Chewpraditkul, IEEE TNS* ***56****, 3800 (2009)*

After correlated TSL and EPR study the "design" of the key processes was proposed:



Consideration of tunneling-driven recombination **provides a physical ground** for the slower scintillation decay component in LuAG:Ce, which can't be explained by thermal detrapping and recombination via conduction band as calculated detrapping times are too long.

Nikl et al, Phys. Rev. B ***76****, 195121 (2007)*

The first innovation step …

RAPID COMMUNICATIONS

PHYSICAL REVIEW B **84**, 081102(R) (2011)

Band-gap engineering for removing shallow traps in rare-earth $Lu_3Al_5O_{12}$ garnet scintillators using Ga^{3+} doping

M. Fasoli,[1] A. Vedda,[1] M. Nikl,[2] C. Jiang,[3] B. P. Uberuaga,[3] D. A. Andersson,[3] K. J. McClellan,[3] and C. R. Stanek[3,*]

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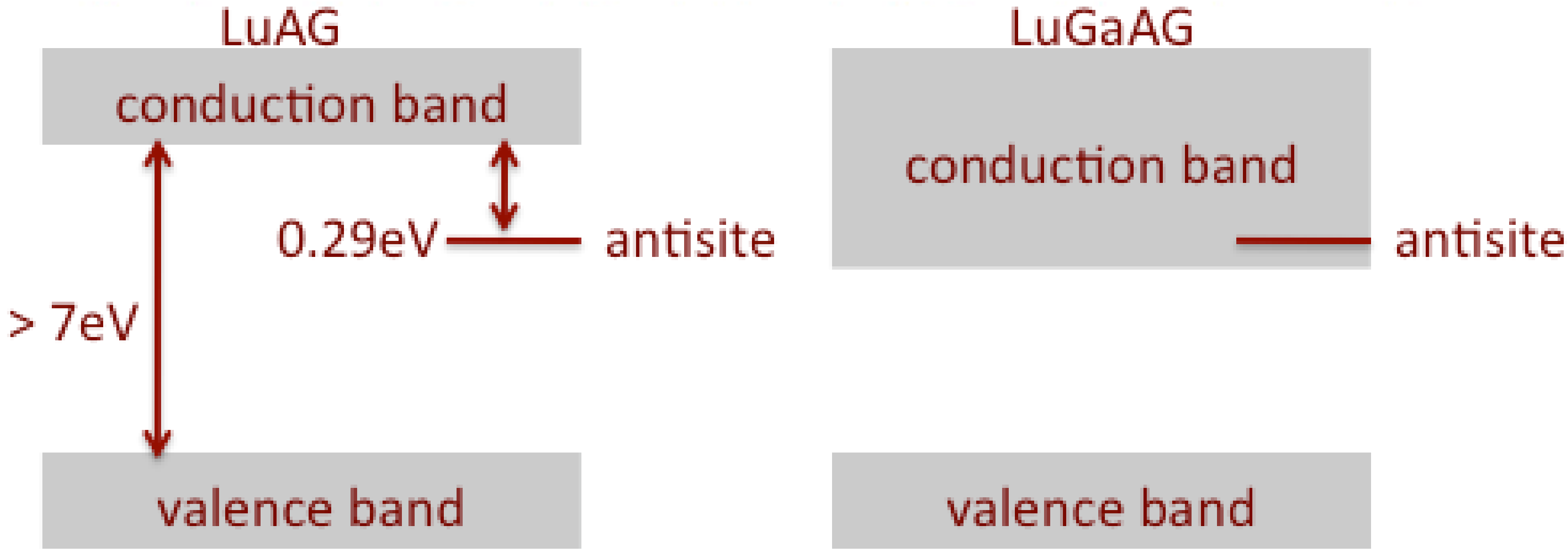
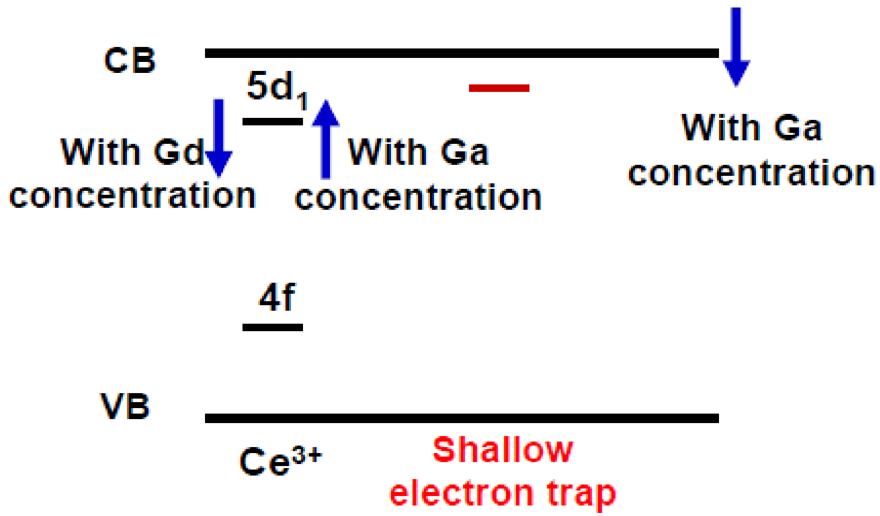
(Received 4 August 2011; published 26 August 2011)



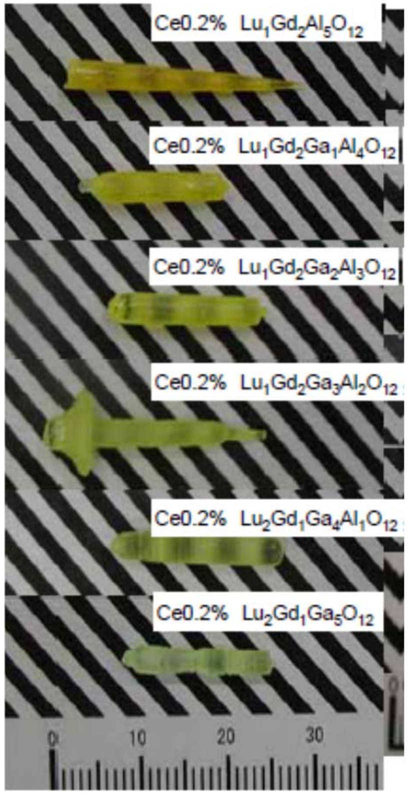
Multicomponent garnets $Gd_yLu/Y_{3-y}Ga_xAl_{5-x}O_{12}$



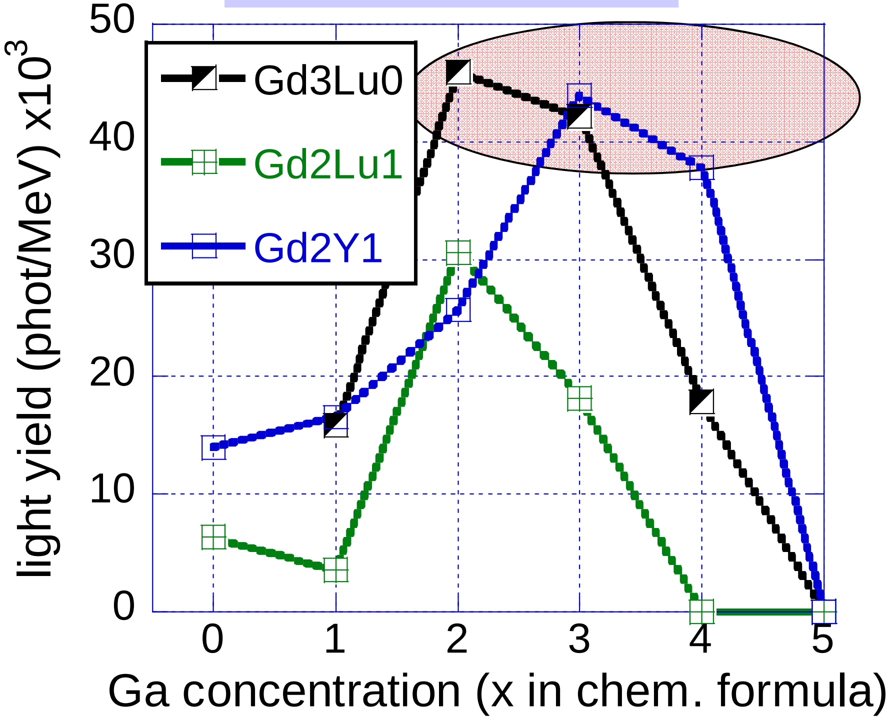
In Ga-admixed LuAG the $5d_1$ level of $Ce(Pr)^{3+}$ gets closer to CB edge ⇒ thermally induced ionization&LY loss

The Gd admixture can help!

Kamada et al, Crystal Growth& Design **11**, 4484 *(2011)*

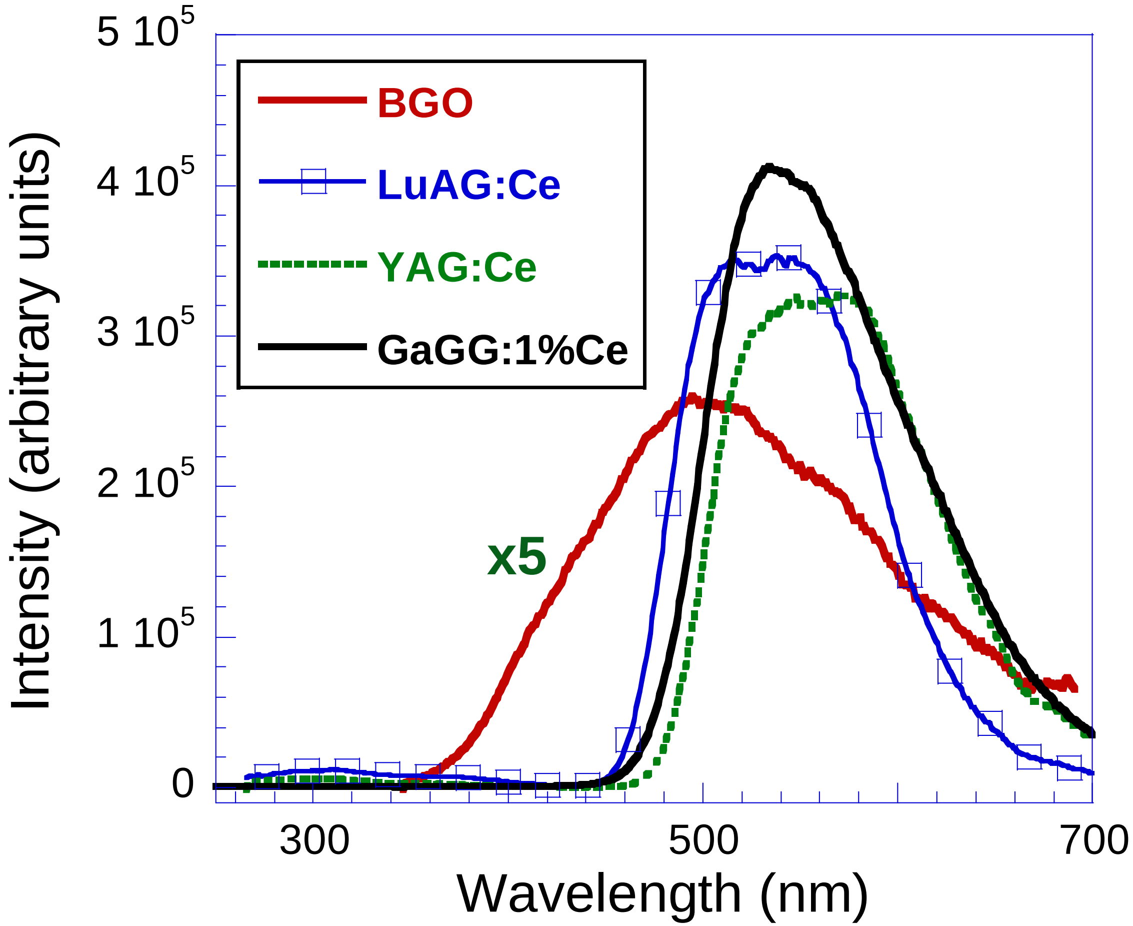


Light yield



LY increase more than twice for x=2-3
Scint. decay dominated by PL decay time for x=3, but contains some slow comp.

RL spectra of Ce-doped YAG, LuAG and GAGG



Kamada et al, . J. Phys. D ***44,*** *505104 (2011)*
Prusa et al, Rad. M eas. ***56****, 62 (2013)*

Scintillation efficiency (integral of RL spectrum) of GAGG:Ce is only about 10-20% higher than that of YAG:Ce and LuAG:Ce, i.e. **huge LY increase shows that the slow part of scintillation response was transformed into fast one**.

The highest LY of GAGG:Ce (spectrally corrected) measured so far is approaching 60 000 phot/MeV (close to theoretical limit, see *Dorenbos, IEEE TNS* ***57****, 1162 (2010))*

Kamada et al, Optical Materials ***36****, 1942 (2014)*

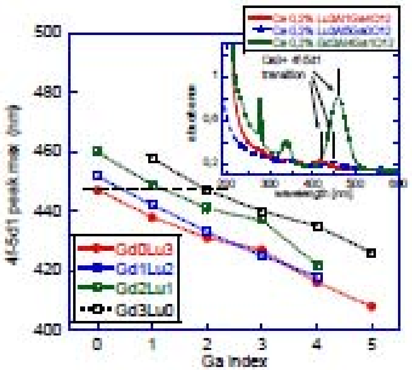
Development of Ce:GAGG and its application

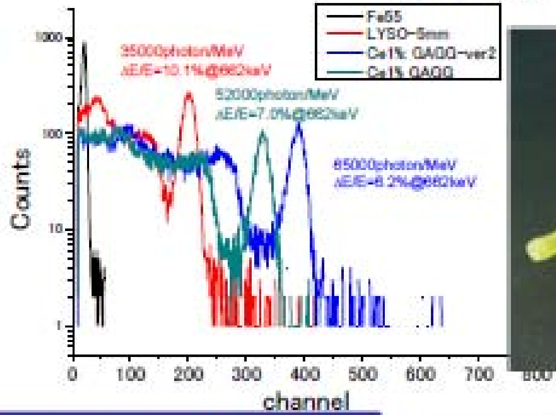
Courtesy of A. Yoshikawa

With Furukawa, JAEA, Univ. Tokyo

Nov. 2010

Ce:Gd$_3$ (Al,Ga) $_5$O$_{12}$





Jan. 2011

development → Luminescent study, LY, Decay evaluation → 2inch crystal !

Nov. 2011 in the market

Just one year

Detector unit

GAGG +APD

Sept. 2012

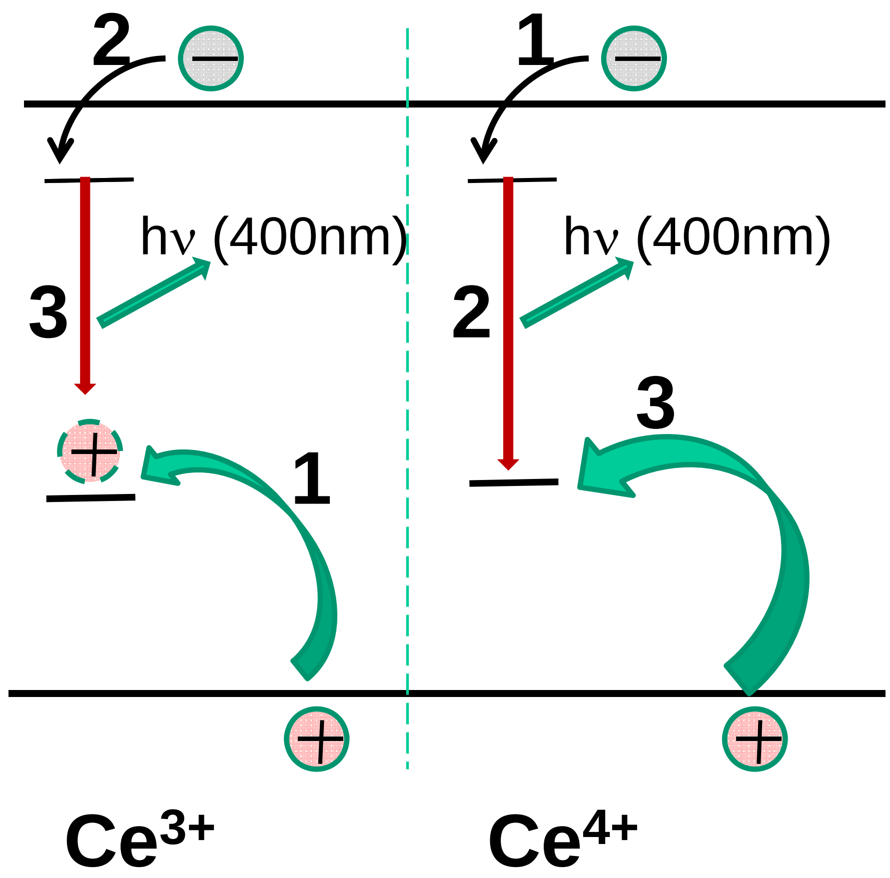
→ Compact & real time Survey meter → Food checking system → GAGG Compton camera on the unmanned helicopter

DE strategy – stable Ce^{4+} center in scintillation mechanism of oxide scintillators

In 1990's it was general opinion that Ce^{4+} is scintillation killer in aluminum perovskite (YAP) host, but we have to change our mind now as far as its role in Ce-doped orthosilicates and garnets …

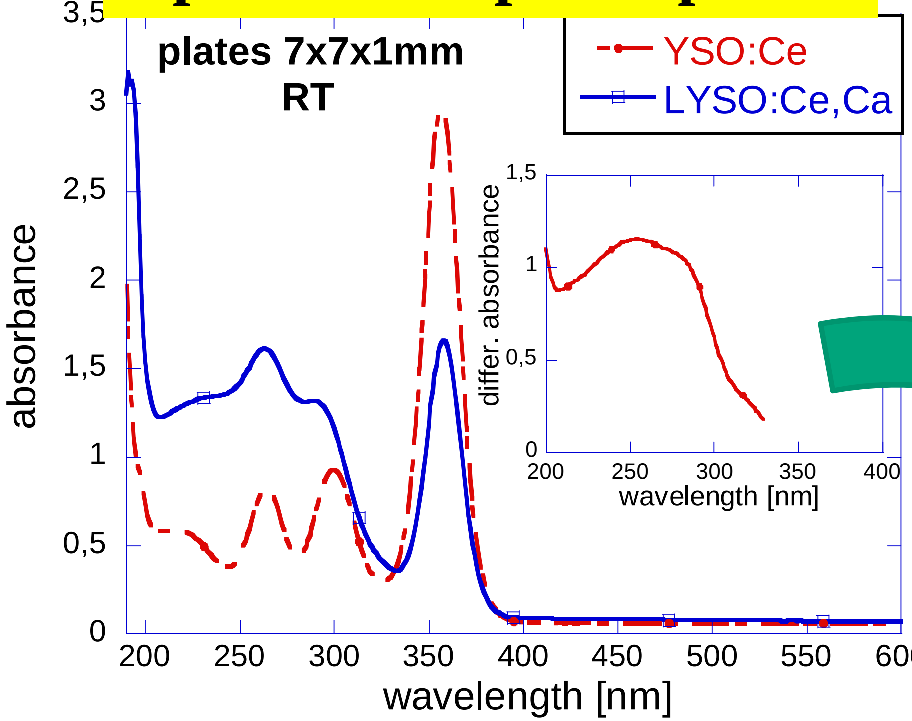
LYSO:Ce,Mg :Blahuta et al, IEEE TNS 61, 3134 (2013)
LYSO:Ce,Ca: Chewpraditkul et al, Opt. Mat. ***35****, 1679 (2013)*

- In LYSO:Ce,Mg, **the Mg^{2+} codoping and air annealing** induce the presence of Ce^{4+} (proved by XANES, optical absorption),
- **LY is enhanced and afterglow strongly diminished also because the oxygen vacancy concentration is diminished!**



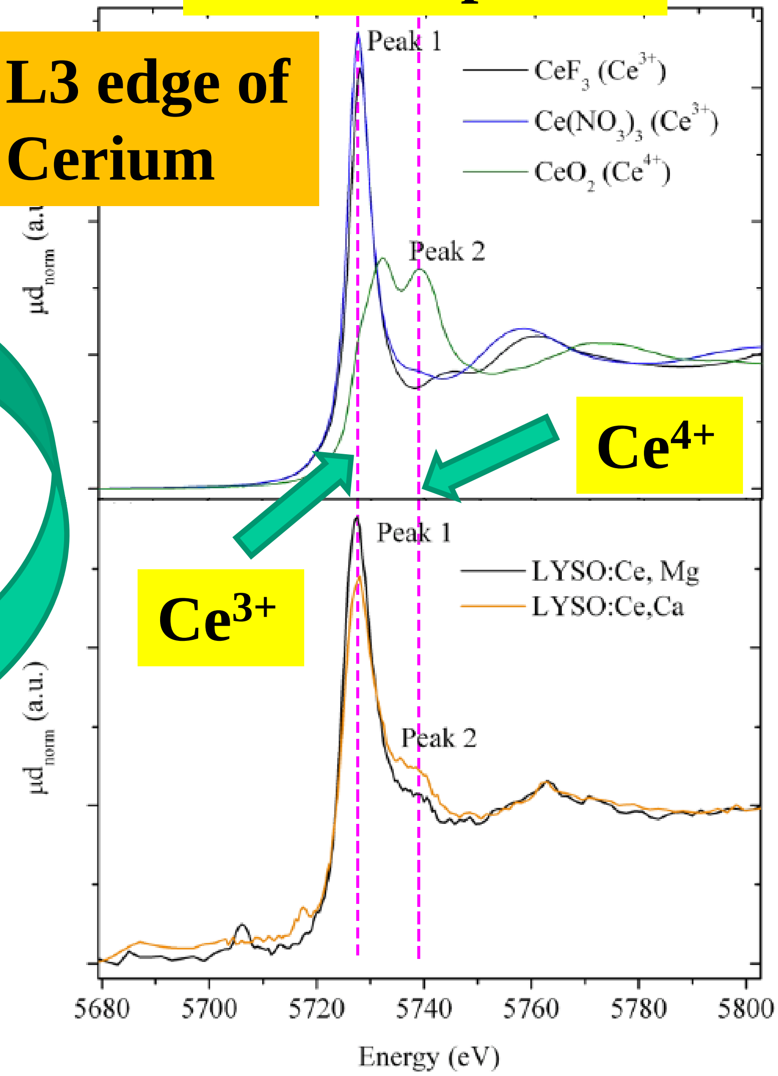
Ce^{4+} center in LYSO:Ce,Me^{2+}

Optical absorption spectra



Charge tranfer (CT) absorption of Ce^{4+}

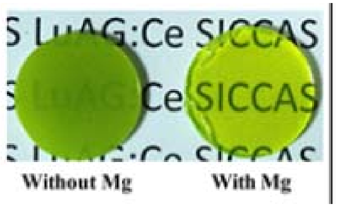
XANES spectra

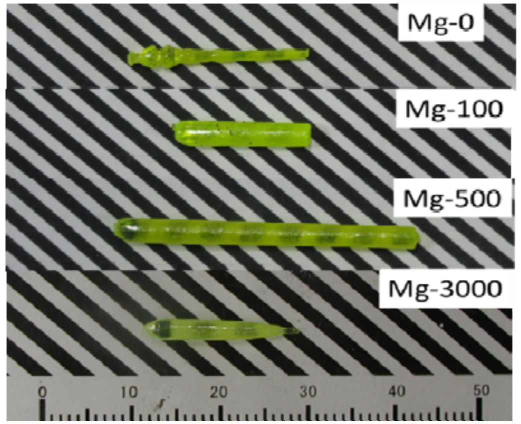


The light yield of about 32,000 ph/MeV was obtained for LYSO:Ce,Ca, which is among the highest ones ever reported in literature. Ca content of about 60 at. ppm was confirmed by GDMS.

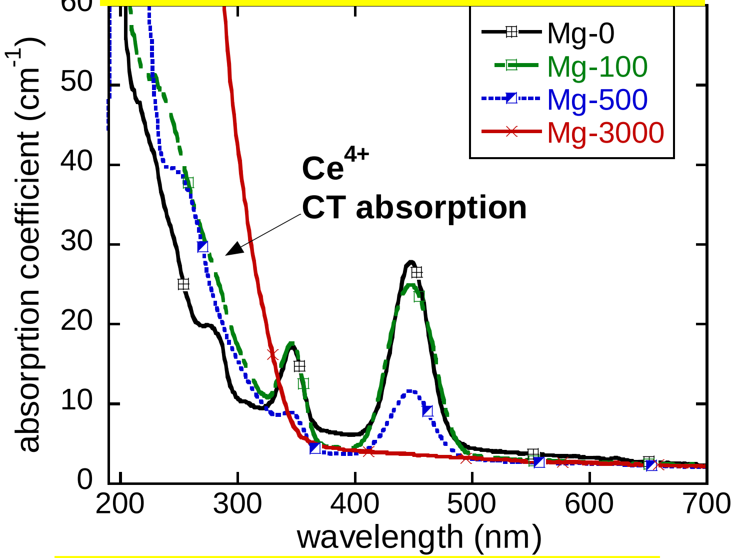
Up to 35% of Ce^{4+} in total Ce content

Mg^{2+} codoped LuAG:Ce: concentration dependence





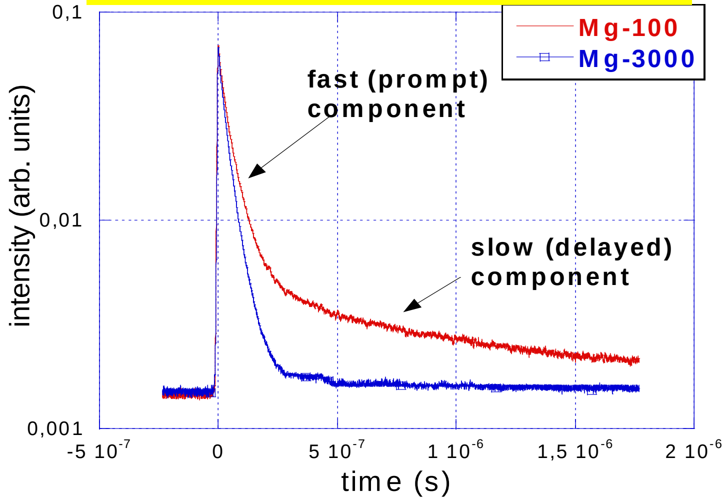
Absorption spectra



OC from SICCAS
mPD crystals from A. Yoshikawa lab

Nikl et al, Cryst.Growth Des. **14**, 4827 (2014)
Liu et al, Phys.stat. sol. RRL **8**, 105 (2014)

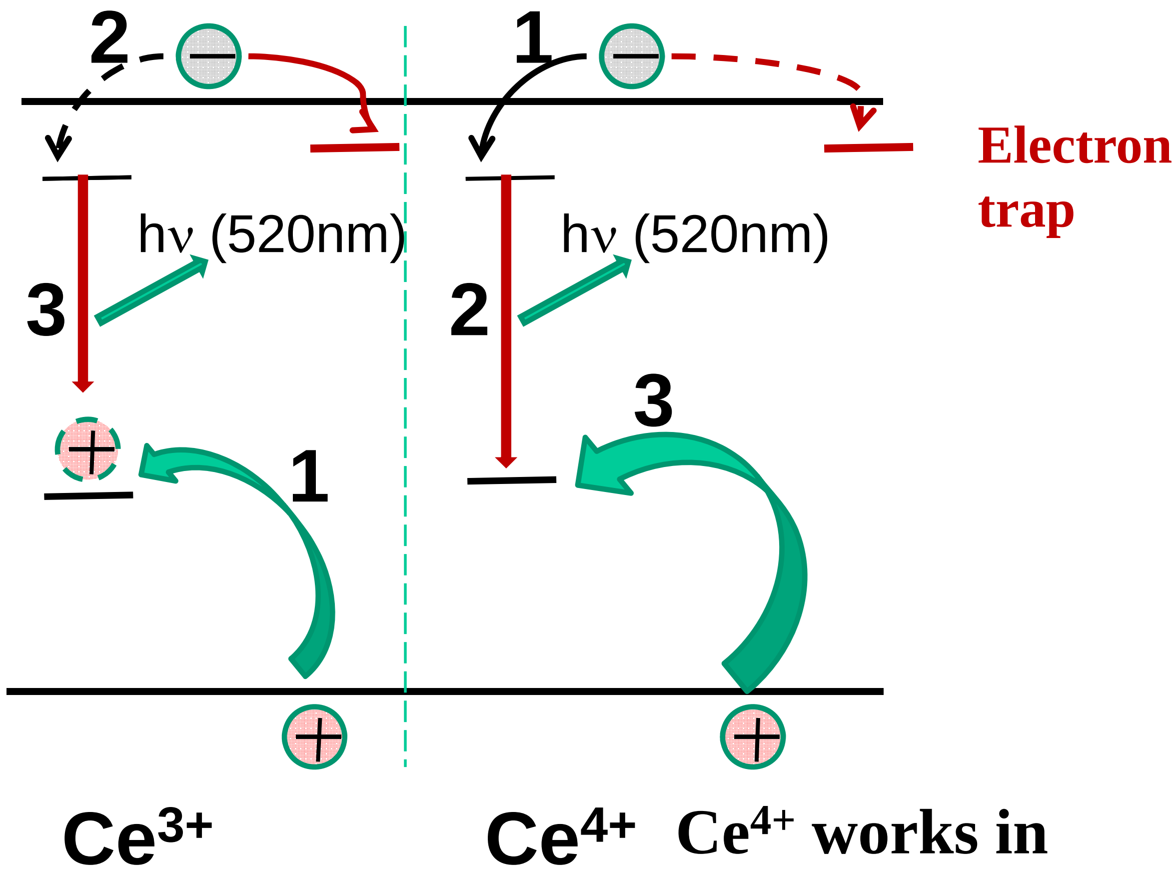
Scintillation decay



Sample	Light yield (ph/MeV)	T1(ns)/ I1(%)	T2(ns)/ I2(%)	Afterglow at 4 ms(%)/400ms(%)
Mg-0	4850	58/48	300/52	19/8.3
Mg-100	23100	48/58	380/42	1.3/0.08
Mg-500*	18800	48/57	275/43	2.5/0.07
Mg-3000	14100	15/11	51/89	0.2/0.03
LuAG-Ce – Cz	17200	58/42	958/58	2.9/0.4

Why stable Ce^{4+} is that good for LY increase in oxide single crystal (ceramic) scintillators

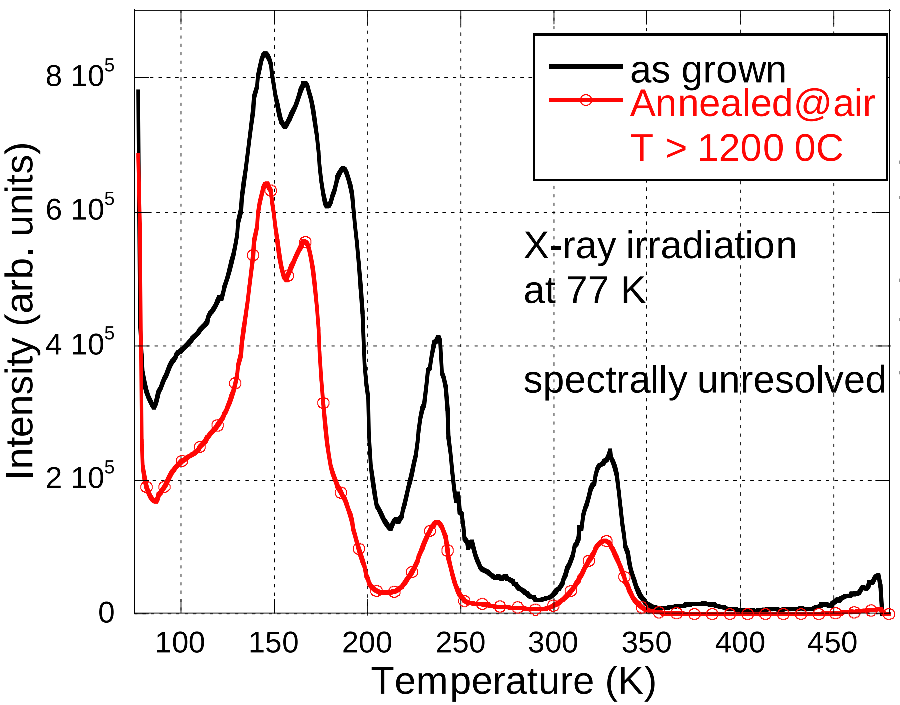
Ce^{4+} center can directly compete with any electron trap for electron capture in the first instants of scintillator mechanism so that **it will directly convert a fraction of slow part of scintillation response to the fast one**. **Ce^{3+} cannot make this as it must capture the hole first.**



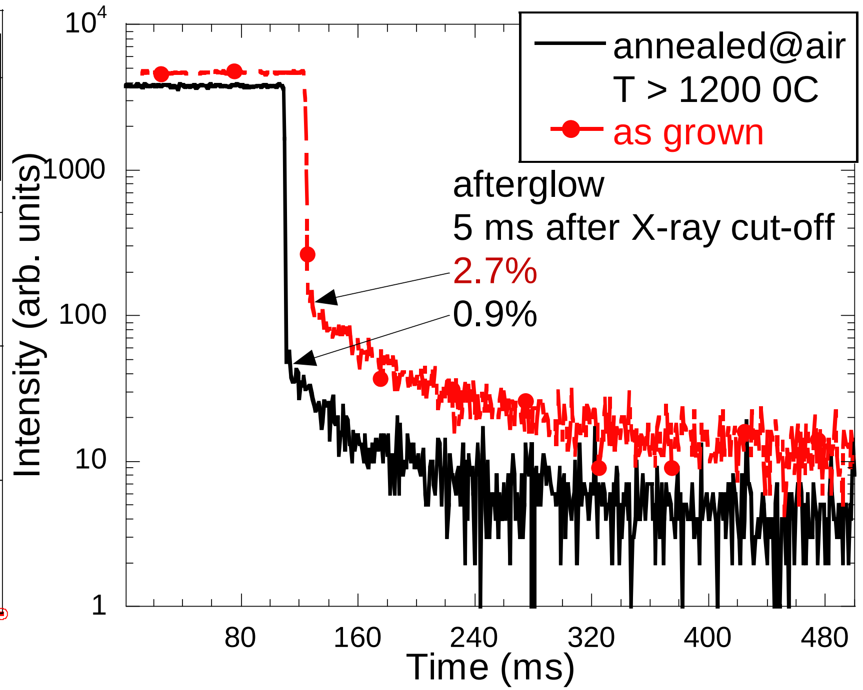
Ce^{4+} works in parallel with Ce^{3+} center, they are not competing!

Annealing in air – LuAG:Ce single crystal

TL glow curves



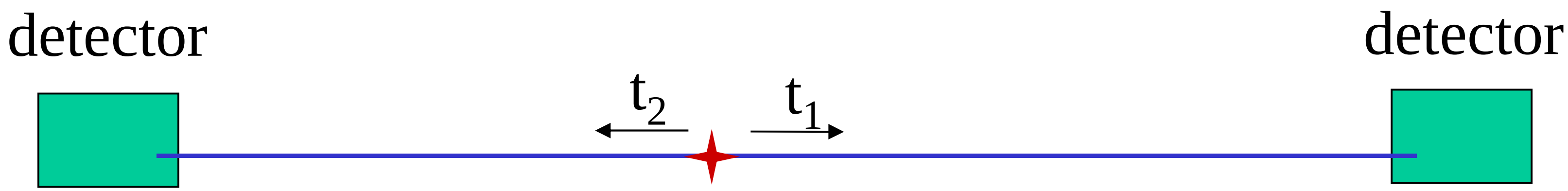
Afterglow

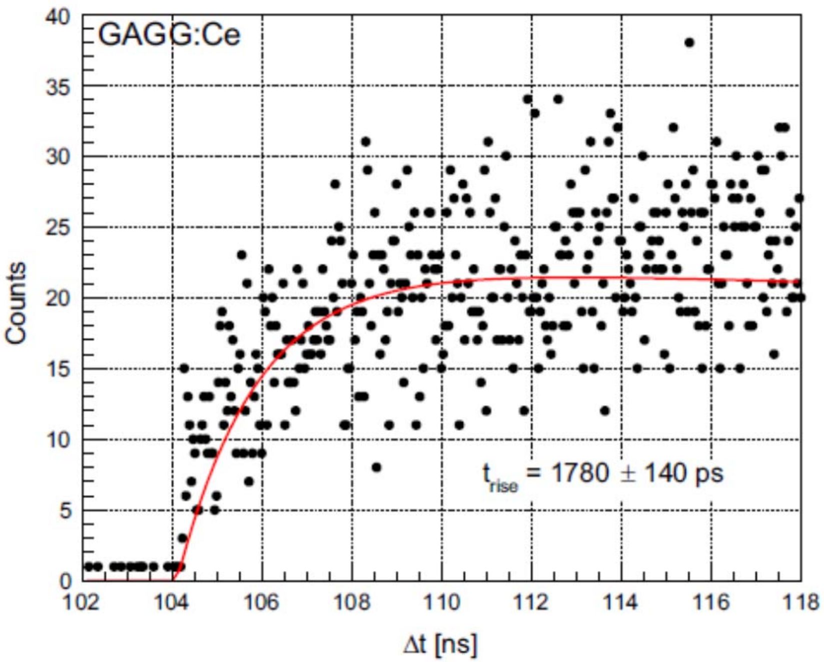


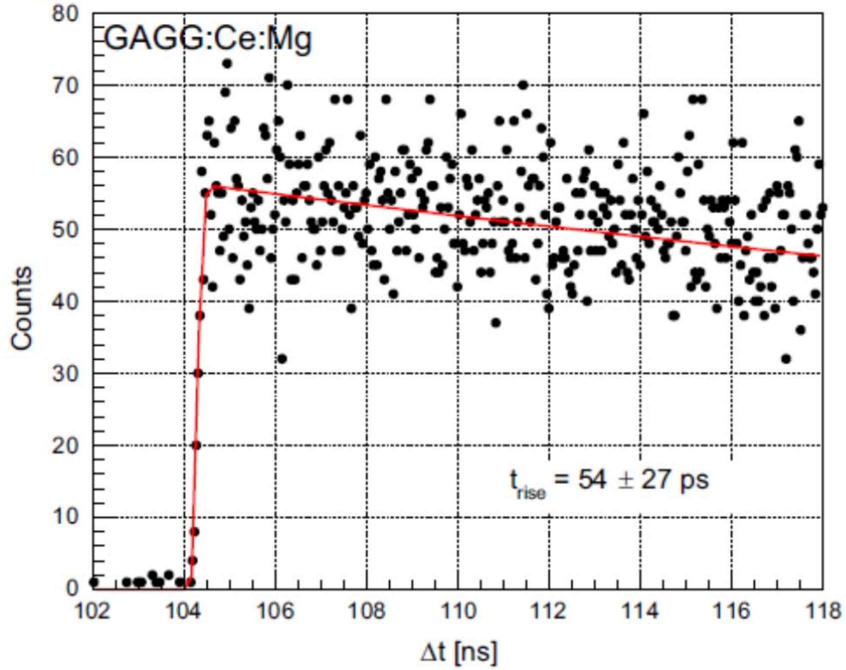
After annealing CT absorption of Ce^{4+} center appears , afterglow decreases and TL intensity significantly decreases - different level of decrease can be observed in first two peaks at 144 K and 167 K compared to those at higher temperature → different origin of traps in both groups. (*Nikl et al, J. Lumin.* . **169**, 539 *(2016))*

Timing coincidence resolution - Mg^{2+} codoped GAGG:Ce

Critical parameter for usage of fast scintillators in time-of-flight measurements



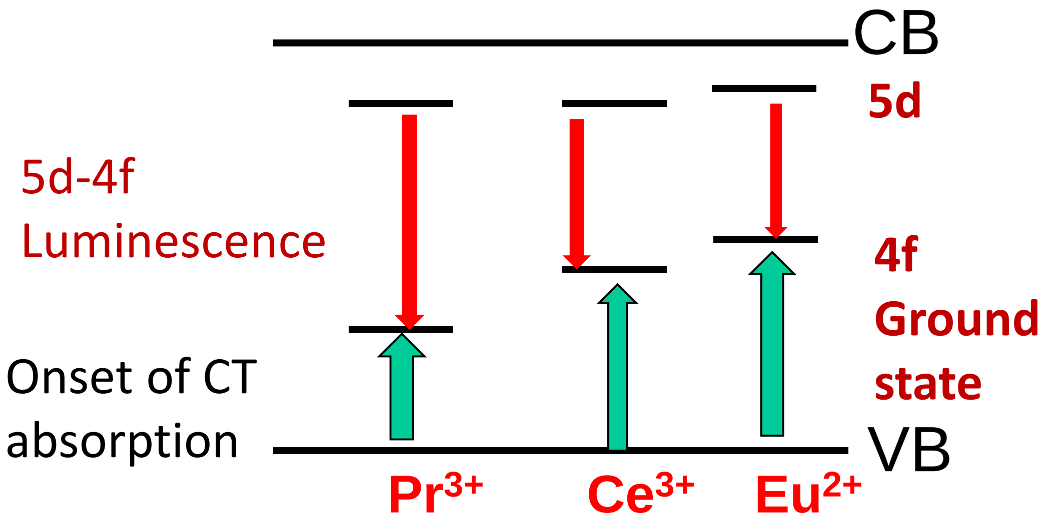




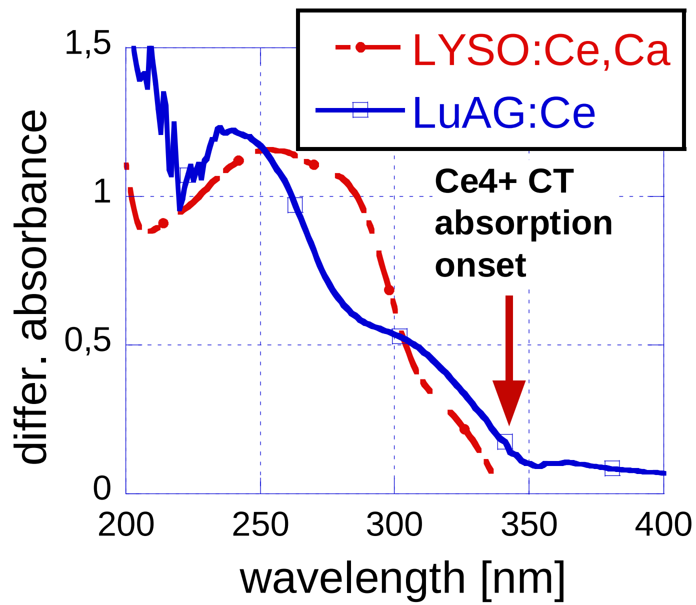
Mg codoping in GGAG:Ce almost erase rise time in scintillation decay and TCR is improved from about 540 ps to 230 ps. Comparable values with LYSO:Ce,Ca ⟹ candidate for PET!!!
(*Lucchini et al, NIM A **816**, 176 (2016)*)

Better quality GAGG:Ce,Mg - TCR of 196 ps was achieved (Kamada et al, IEEE TNS 63,443 (2016)

Ce^{4+},Pr^{4+} in LuAG, YAP, LYSO hosts



Charge transfer absorption of Ce^{4+}

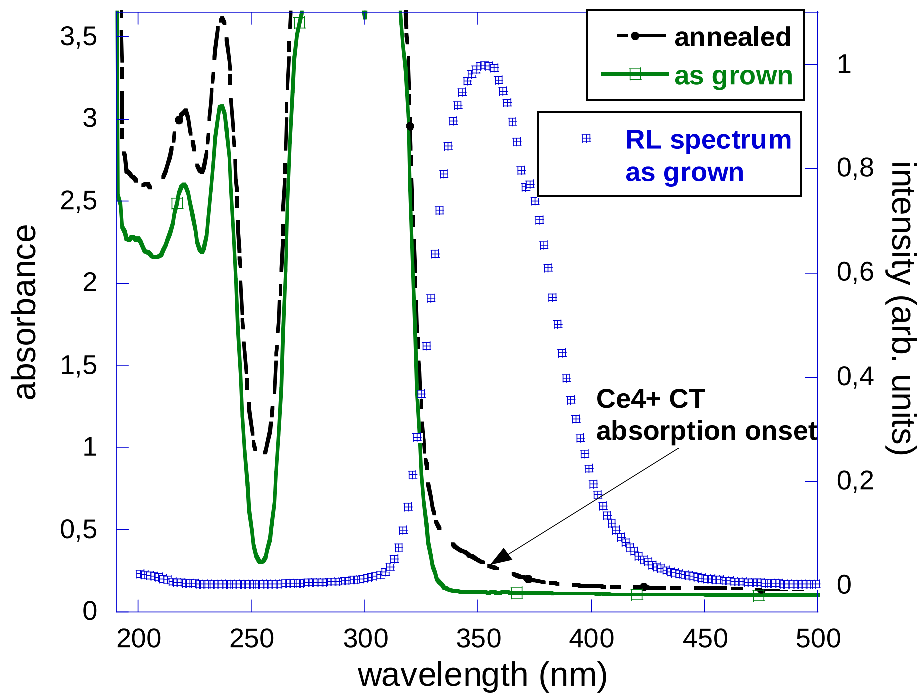


Nikl et al, Optical Materials **26**, *545* (2004)

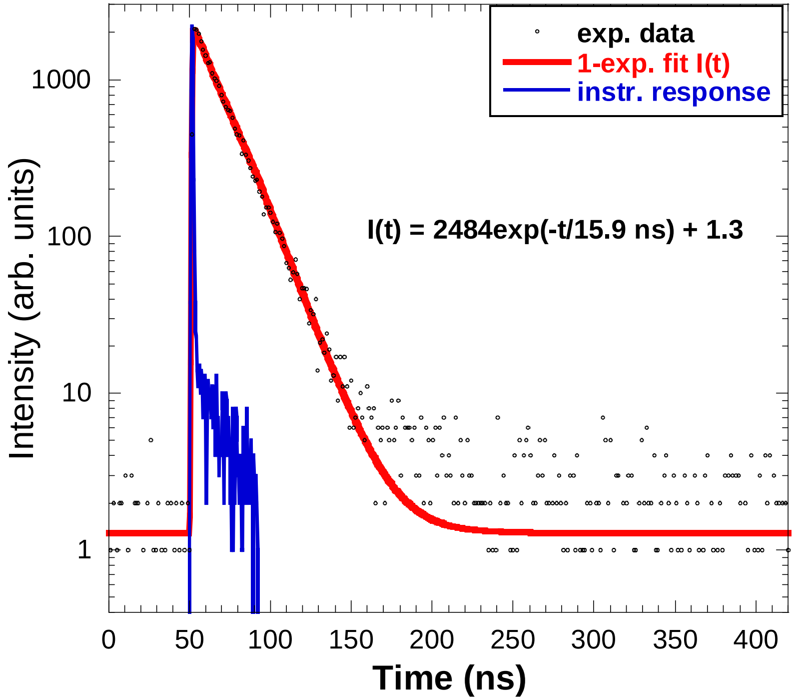
CT absorption of Ce^{4+} (Pr^{4+},Eu^{2+}) is analogous to well-studied CT of Yb^{3+}. Within the class of materials constituted by the same anion (e.g. oxides, fluorides) its onset will be very similarly positioned. For the Ce^{4+} center in garnet, silicate and perovskite oxide hosts it will be positioned around 340-350 nm. **Thus it will re-absorb scintillation of Ce^{3+} in YAP, but will not in silicates and garnets**. Energy transfer from Gd^{3+} sublattice towards CT absorption of Ce^{4+} might be one of the reasons of decrease of LY in GGAG:Ce,Mg

Ce^{4+} center in YAP

Absorption and emission spectra of Ce^{3+} in YAP



Photoluminescence decay of Ce^{3+} in YAP

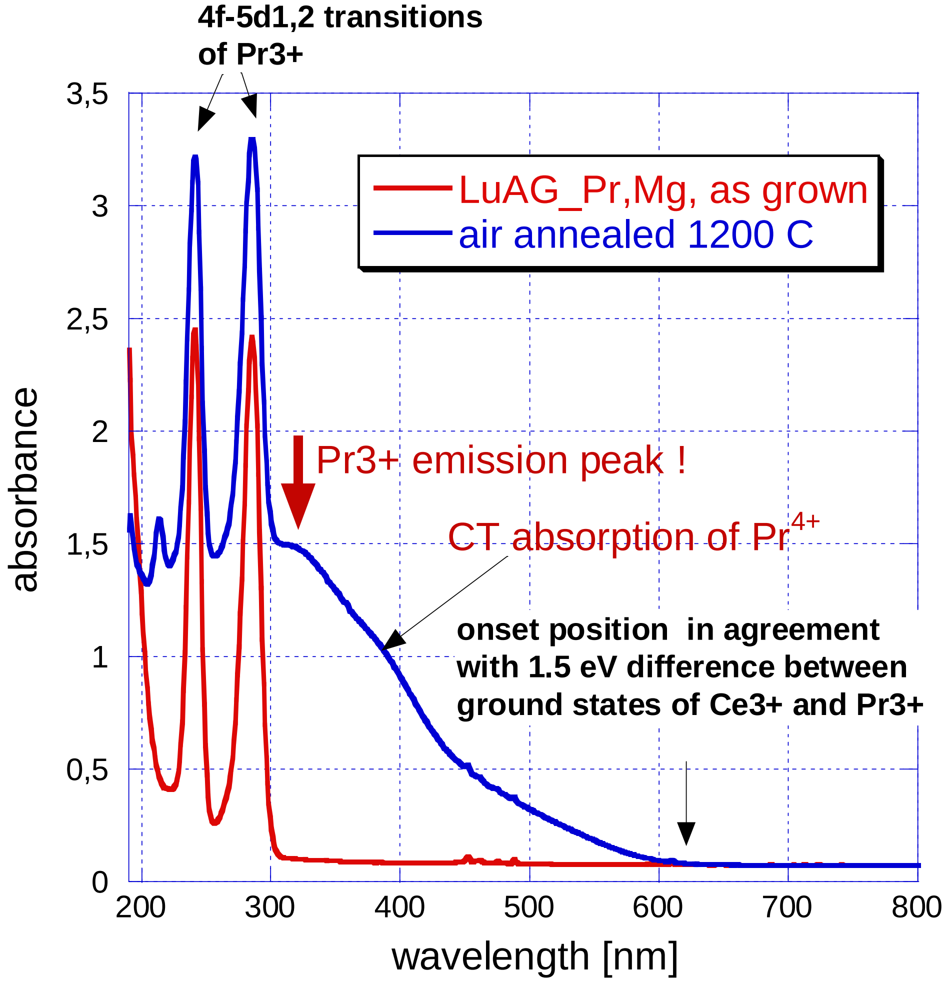


Notable overlap of Ce4+ absorption with emission band of Ce3+ is demonstrated (on the left, 1 mm thick plate), in 1 cm thick sample it will cause reabsorption losses up to 90%.

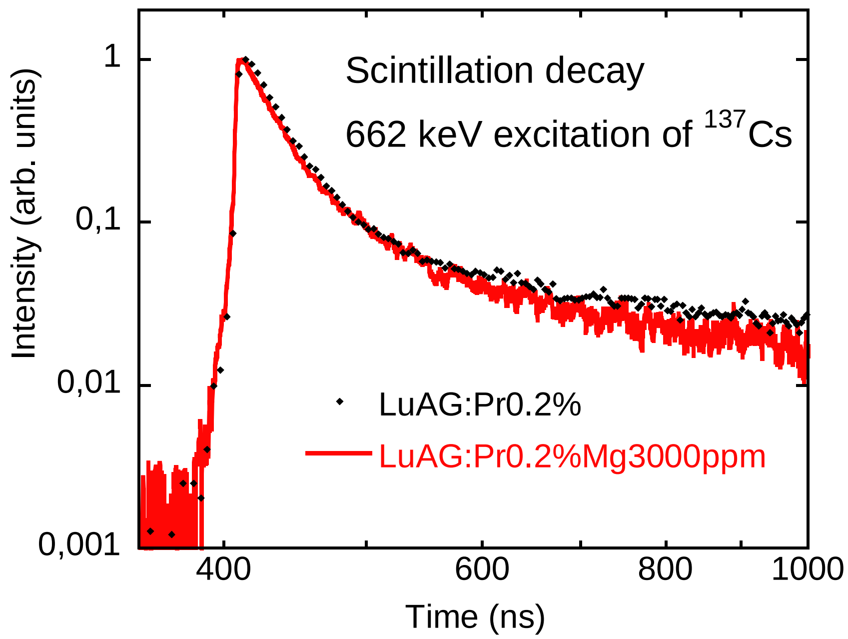
At the same time the nonradiative energy transfer from 5d1 excited state of Ce3+ towards CT absorption band is not substantial as only little shortening of PL decay time is observed up to 10% (on the right).

Does Pr^{4+} help?
Not in oxides!

Absorption spectra LuAG:Pr,Mg, 1 mm thick

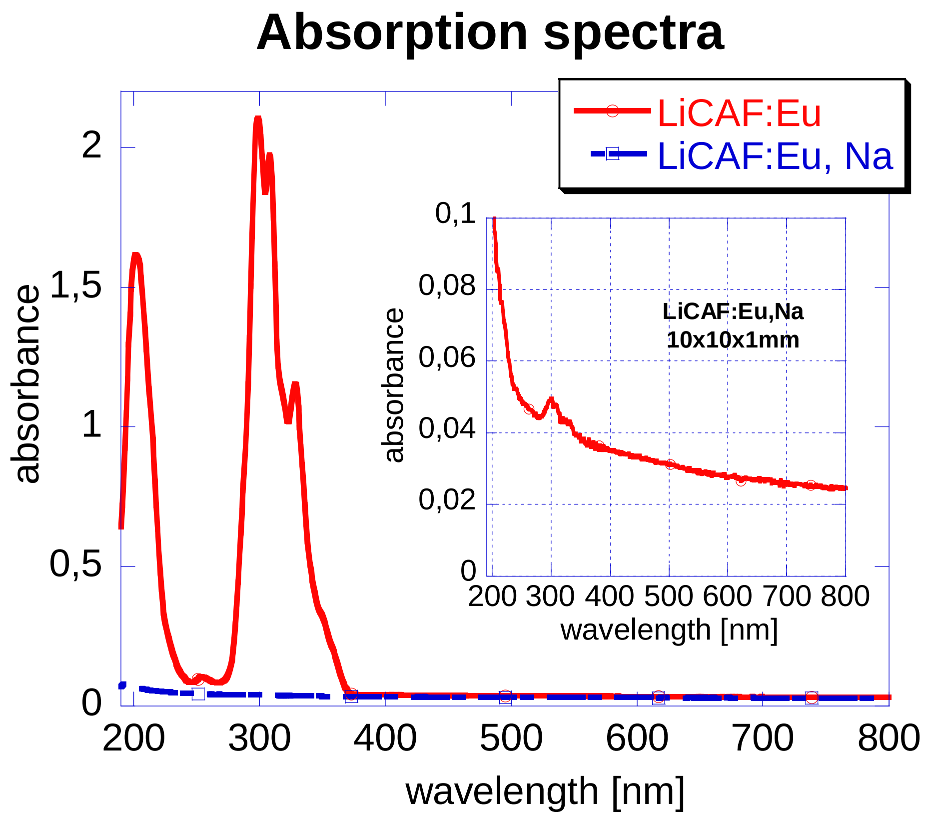


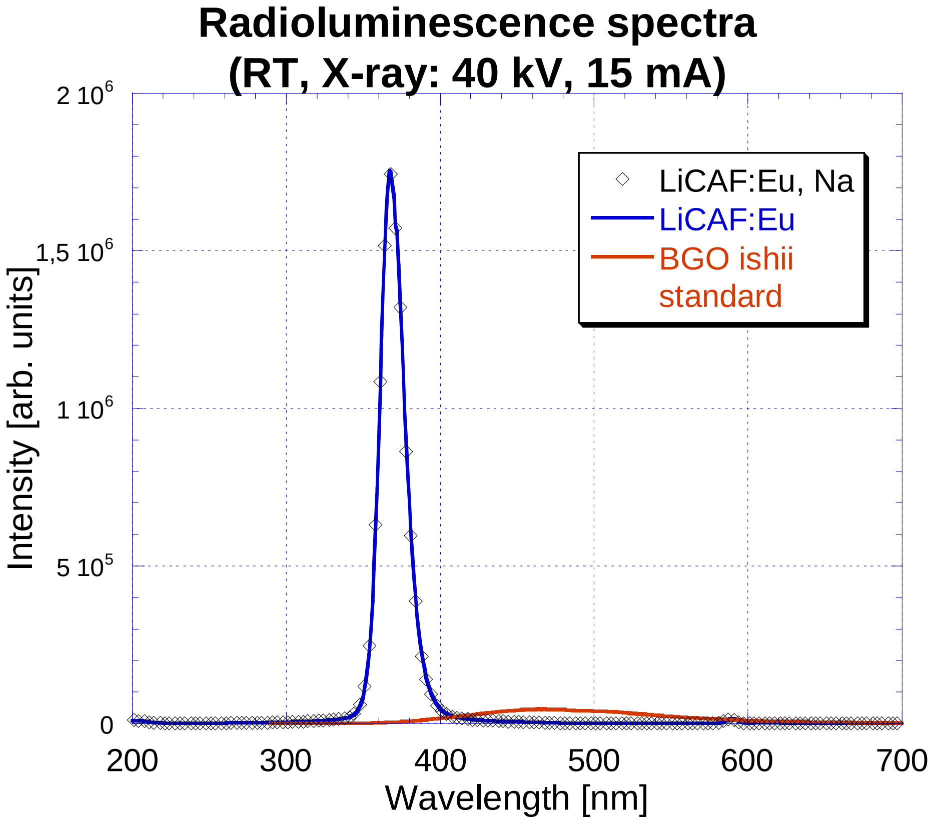
Total overlap of Pr^{4+} CT absorption and Pr^{3+} emission spectra causes significant reabsorption of scintillation light and disable usage of this concept for the **bulk** Pr-doped oxide materials!



Trends in scintillation decay are the same as in Ce,Mg-doped LuAG
Pejchal et al, J. Lumin. accepted

Eu-doped $LiCaAlF_6$ single crystal





Na codoping almost erases stable Eu^{2+} center (converting it into Eu^{3+} to re-establish charge balance), but radioluminescence spectra in both samples shows closely similar absolute intensity of the emission belonging to Eu^{2+}.

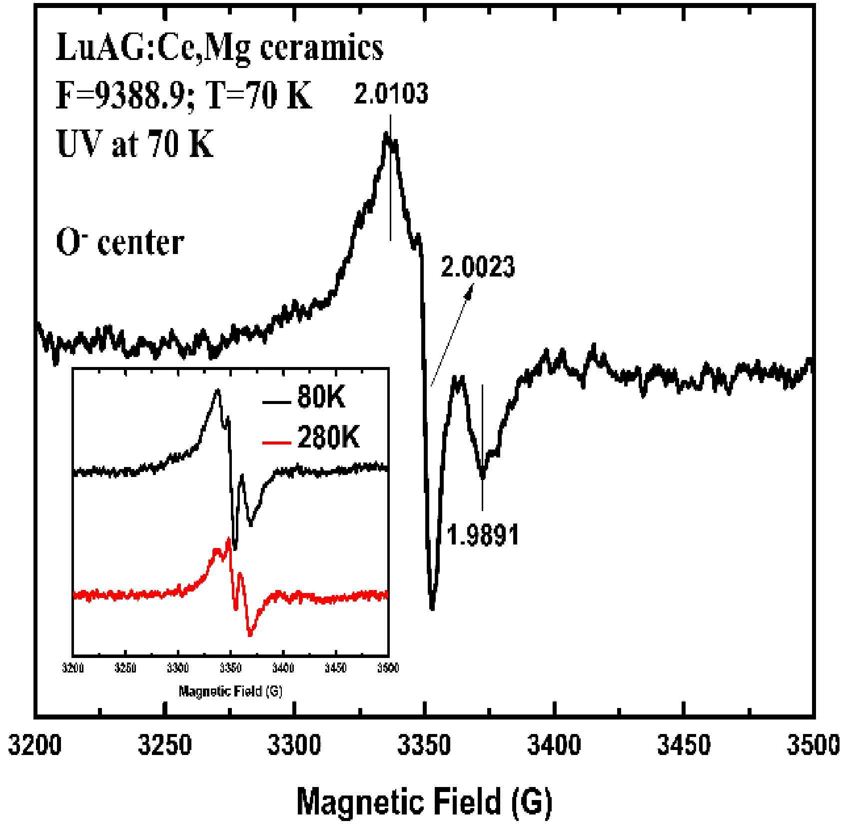
Thus, situation is completely analogous to the Ce^{3+} - Ce^{4+} conversion in silicates or garnets reported before.

LY increase not so expressed in this case due to complex situation in charge traps in LiCAF

*Nikl et al, Appl. Phys. Letters **102**, 161907 (2013)*

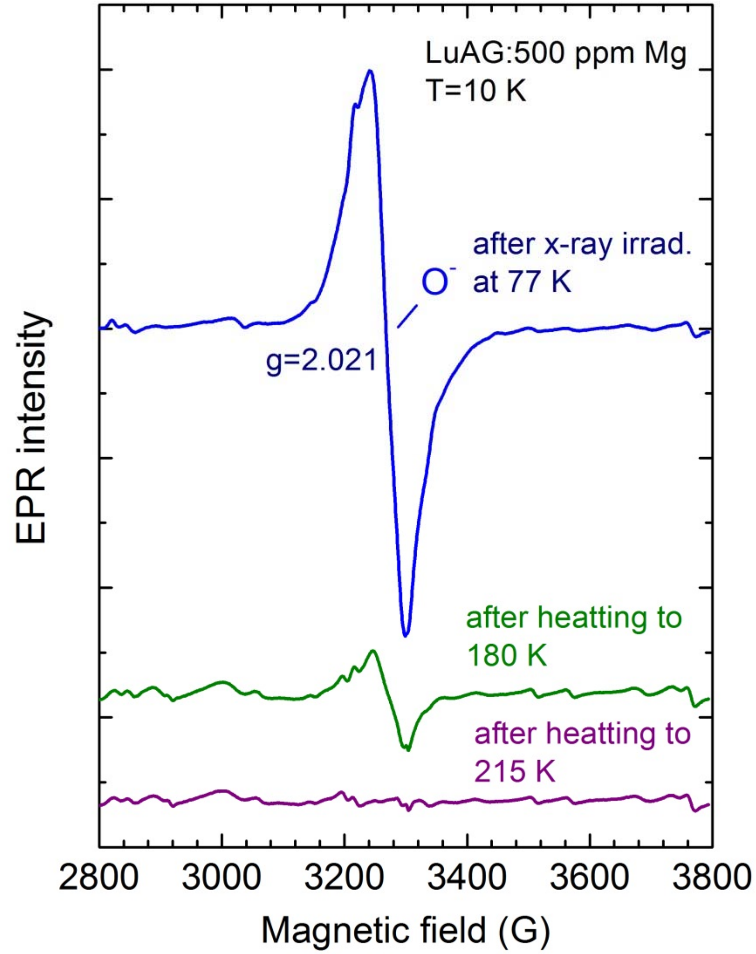
EPR signature of O^- hole center – work in progress

In LuAG:Ce,Mg ceramics



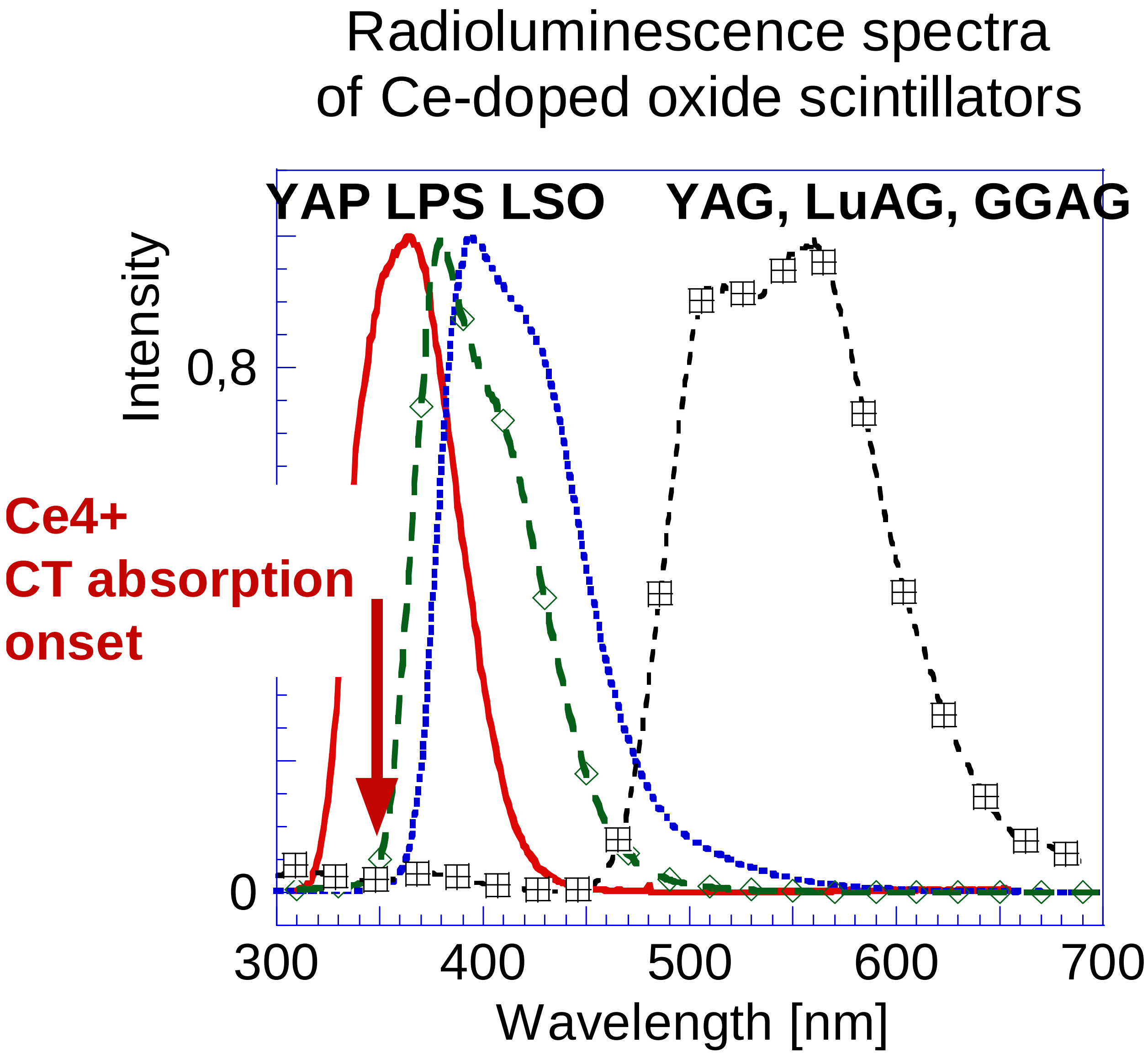
Hu et al, Phys. Stat. Sol. RRL **9**, 245 *(2015)//*
Optical Materials ***45*** *(2015) 252*
Nikl et al, IEEE TNS **63**, 433 (2016)

In LuAG:Eu,Mg single crystal



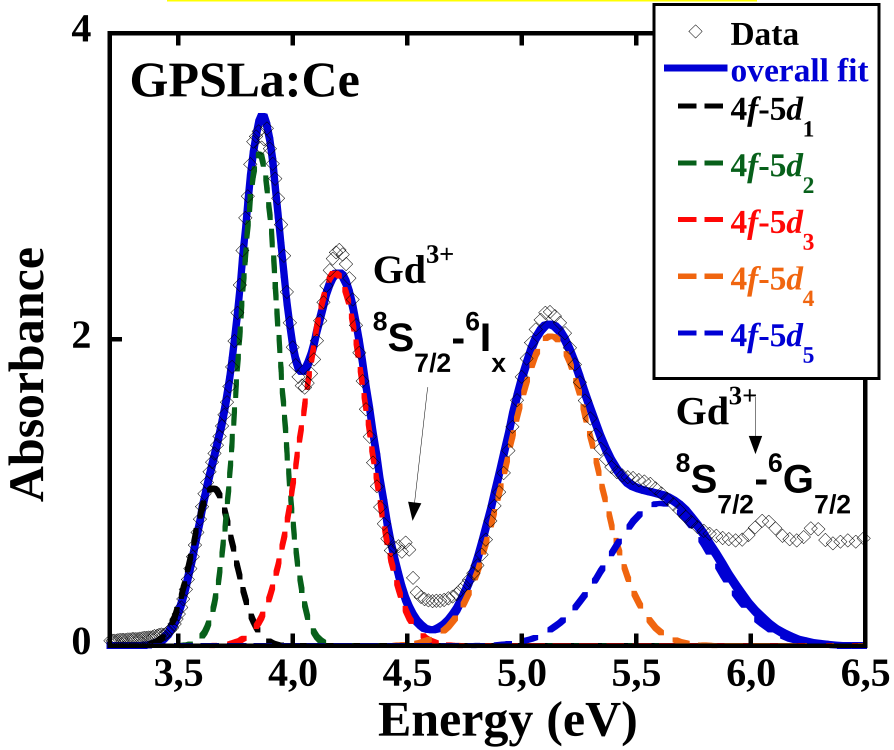
EPR O^- signal can be correlated with TSL glow curves !

A new research topic – the effect of stable Ce^{4+} occurrence in Ce-doped oxide scintillators

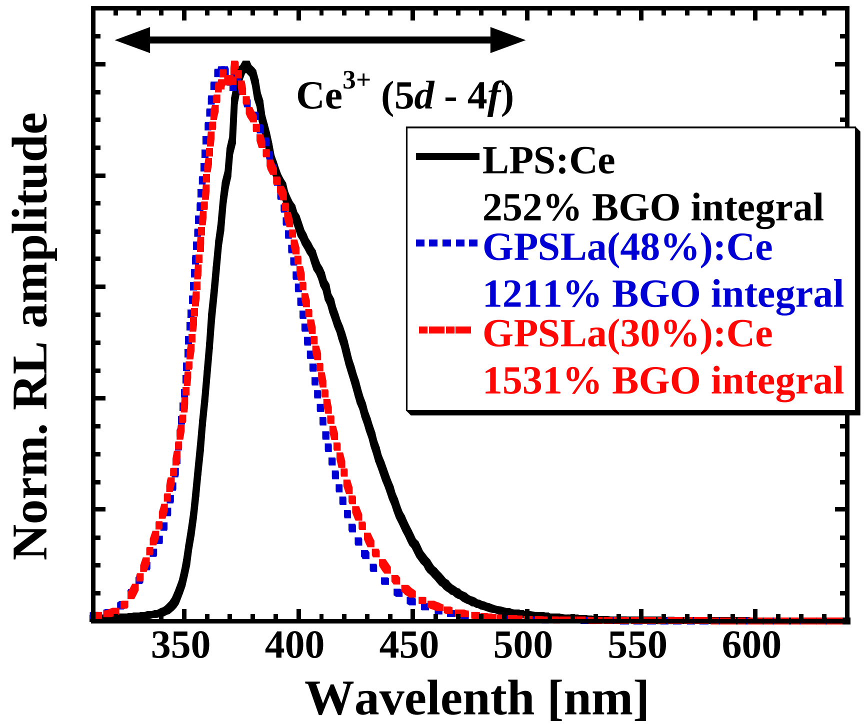


BGE strategy - La-admixed $Gd_2Si_2O_7$:Ce single crystal

Absorption spectra



Radioluminescence spectra

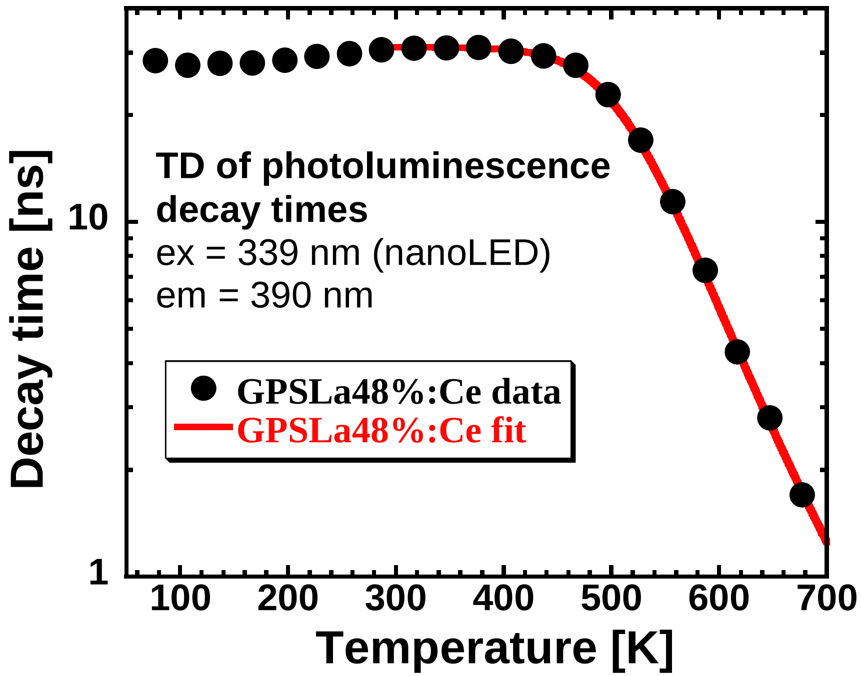


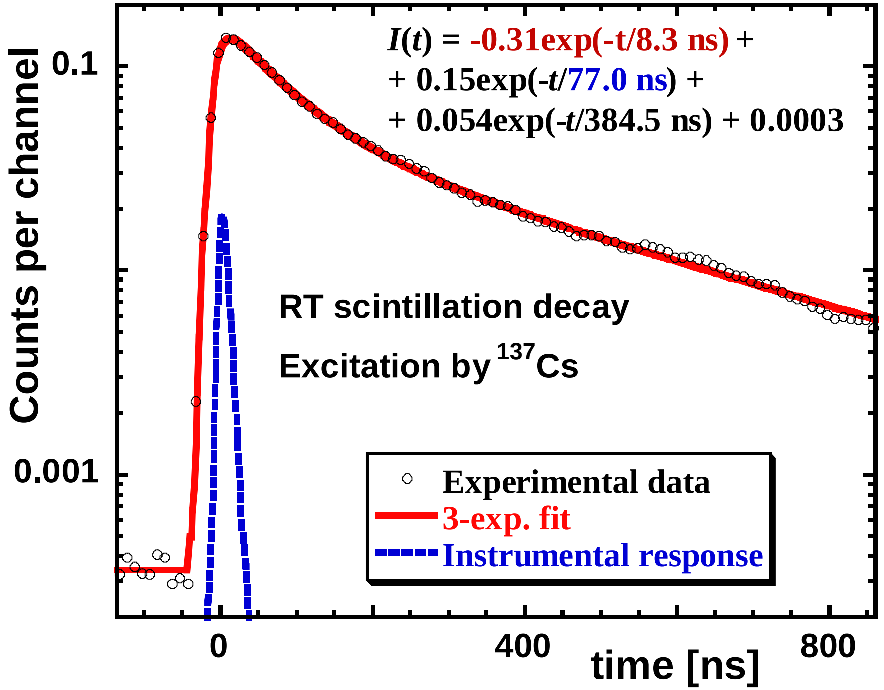
Crystal field splitting of Ce3+ 4f-5d1 levels is lower than in LPS:Ce

*Jary et al., J. Phys. Chemistry C **118**, 26521 (2014)*

Scintillation efficiency (radioluminescence intensity) highest among all the silicate scintillators

Temperature stability, scintillation decay and afterglow of (La,Gd)PS:Ce





Ce^{3+} emission center stable up to 230 ^{0}C, scintillation decay shows a rise time (8-10 ns), leading decay time 70-80 ns, LY> 35 000 ph/MeV, afterglow comparable with BGO!

Czochralski grown crystals of 2” diameter prepared at A. Yoshikawa laboratory, IMR, Tohoku university

Kurosawa et al, Nucl. Instr. Meth. A ***772,*** *72 (2015)*

SCINT 2015: applications in HEP – $PbWO_4$, CeF_3 comeback!

O6-5 Cerium Fluoride - a Radiation-Hard Scintillator for Calorimetry at the HLLHC
F. Nessi-Tedaldi

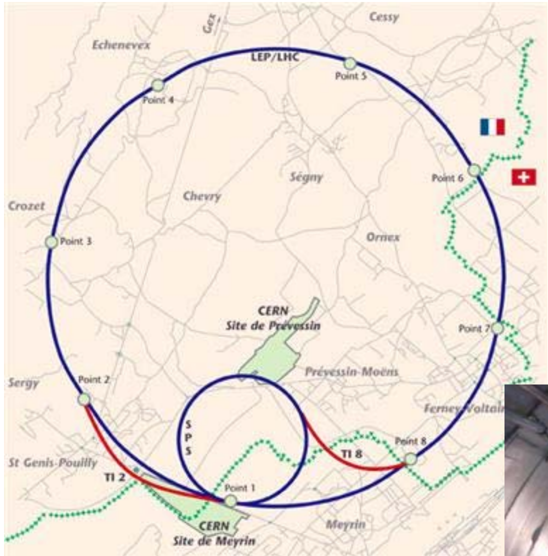
O11-1 Final Concept and Performance of the Electromagnetic Target Calorimeter of the PANDA Detector at FAIR Based on PbWO4
R. W. Novotny

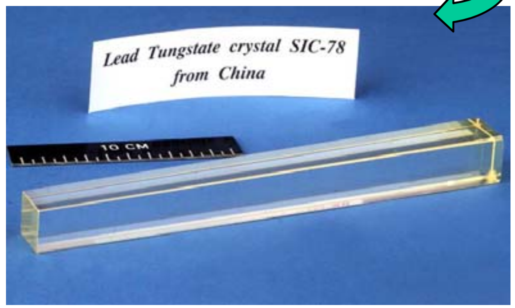
O12-2 Beam Test Results for a Tungsten-Cerium Fluoride Sampling Calorimeter with Wavelength-Shifting Fiber Readout
F. Pandolfi

$PbWO_4$ production restarted in CRYTUR and SICCAS!

High energy physics in 1990's and $PbWO_4$ single crystals

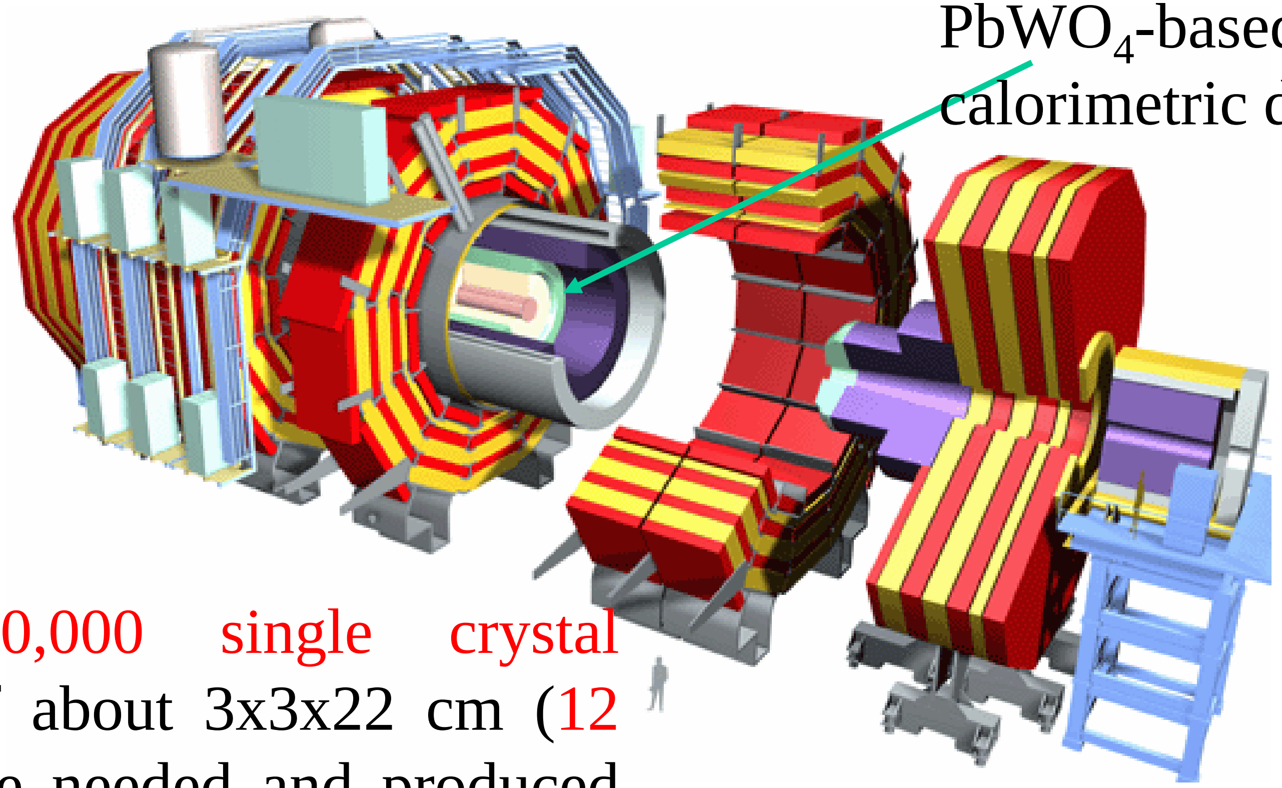
The driving force for R&D in scintillator field was coming from High Energy Physics as they planned new super-accelerator construction in CERN, so called Large Hadron Collider in CERN. At the accelerator ring there are four detectors: ATLAS, CMS, ALICE a LHCb, except ATLAS all others are using scintillators based on single crystals of $PbWO_4$, in total some 15 m^3 composed of nearly 100 000 segments





100 m under the ground, 8.5 km diameter and 27 km long is the accelerator tunnel

Compact Muon Solenoid detector in LHC



$PbWO_4$-based calorimetric detector

about 80,000 single crystal blocks of about 3x3x22 cm (12 m^3) were needed and produced in Russia and China

The search for Higgs boson … **found in 2012!**

The Nobel Prize in Physics 2013
François Englert and Peter W. Higgs
"for the theoretical discovery of a mechanism that contributes to our understanding of the origin of mass of subatomic particles”

SCINT2015: Dark matter detectors

O2-1 (invited) Shedding Light on Dark Matter
P. Di Stefano, *Queen's University, Canada*

- Registration of rare events from cosmic radiation deep underground (Gran Sasso in Italy)
- Search for “double-readout” materials which would be able **at mK temperature to work as scintillators and bolometers at the same time (**Bolometer – a device registering a heat (phonon) generation in a material)
- Suming the light scintillation signal and heat signal can provide a **total energy deposit** in the material!
- Materials with extremely **low intrinsic radioactivity** are needed, e.g. $CaMoO_4$, TeO_2, etc.

O11-2 The Dual Light-Emitting Crystals for WIMPs Direct Searches
X. Sun, et al
O11-3 Scintillation and Phonon Measurement of a $^{40}Ca^{100}MoO_4$ Crystal for AMoRE Double Beta Decay Experiment
J. H. So et al

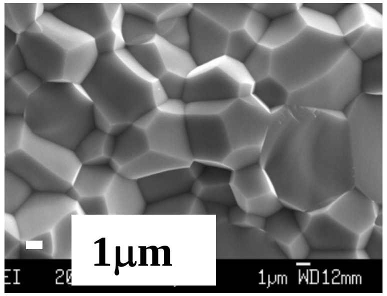
LuAG:Ce,Mg ceramics: Optimization

$(Lu_{1-x-y}Ce_xMg_y)_3Al_5O_{12}$: x=0.3%, y=0.1~0.6%

Starting materials >99.99% purity

Solid-state reaction method

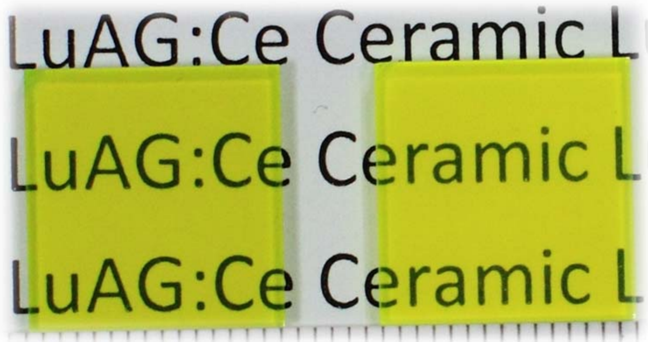
Air-annealing treatment



SEM picture of fractured ceramic surface

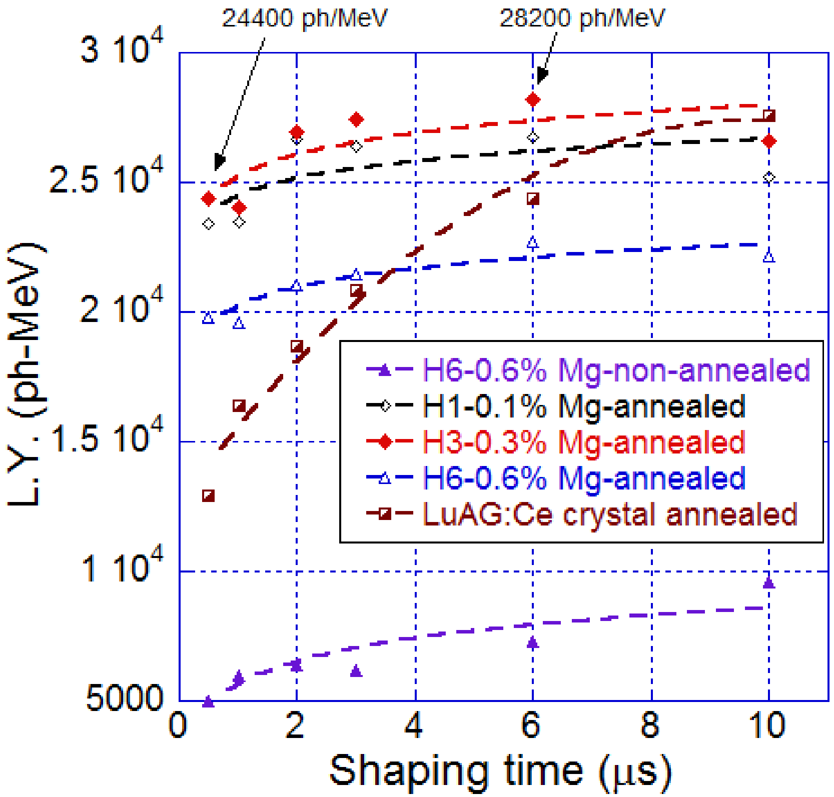
Ball milling, Dry and Sieving → Dry Pressing ~5MPa → Cold Isostatic Pressing ~250MPa → Vacuum Sintering ~1850ºC → Air Annealling ~1450ºC, 20h

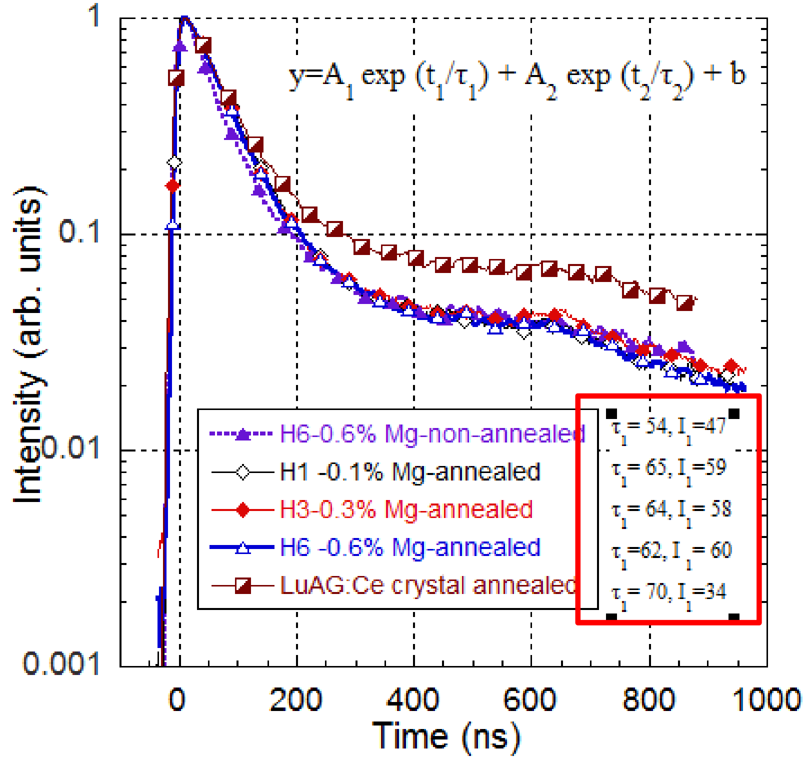
→



T%@550nm >70% 2mm thick

Scintillation performance of LuAG:Ce,Mg ceramics





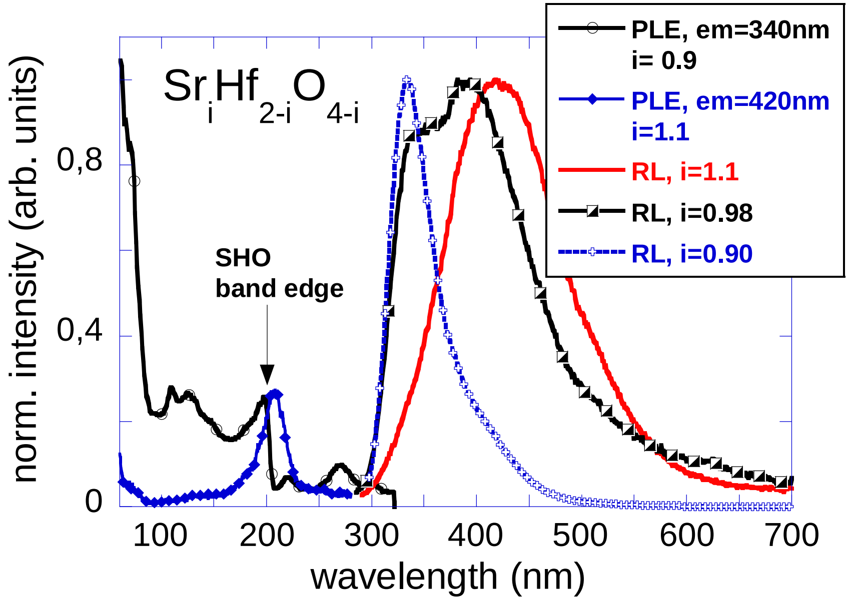
- Compared with LuAG:Ce single crystal, LuAG:Ce,Mg ceramics show: Higher light yield & Faster scintillation decay & Lower slow component!!!
- The highest LY was obtained when 0.2-0.3% Mg^{2+} was introduced.

Liu et al, Adv. Opt. Mater. ***4****, 731 (2016)*

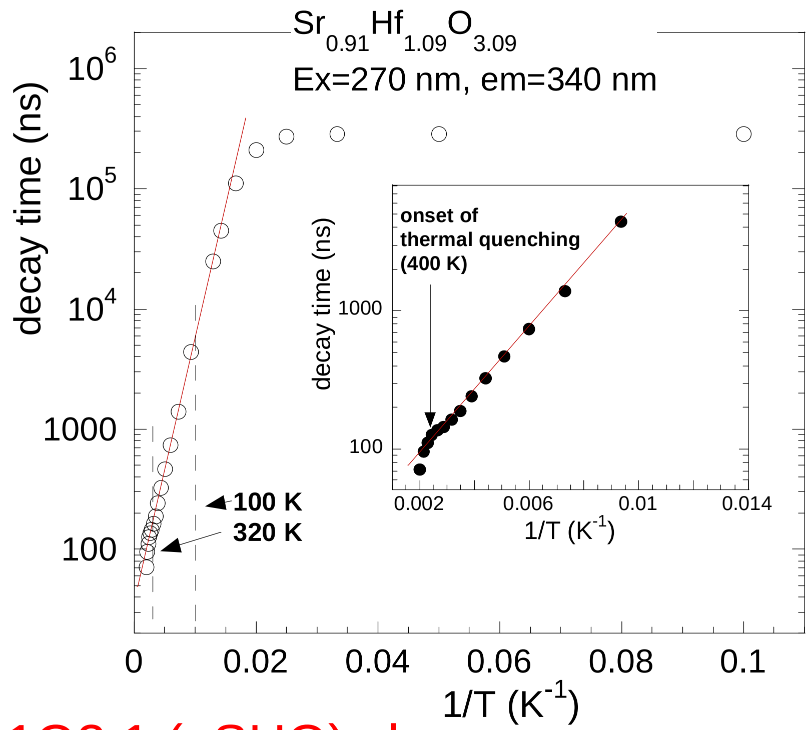
$SrHfO_3$-based scintillators

Studied mostly Ce^{3+} doped as powders or translucent ceramics,
We found efficient scintillation in non-stoichiometric composition

Photoluminescence spectra



Photoluminescence decays

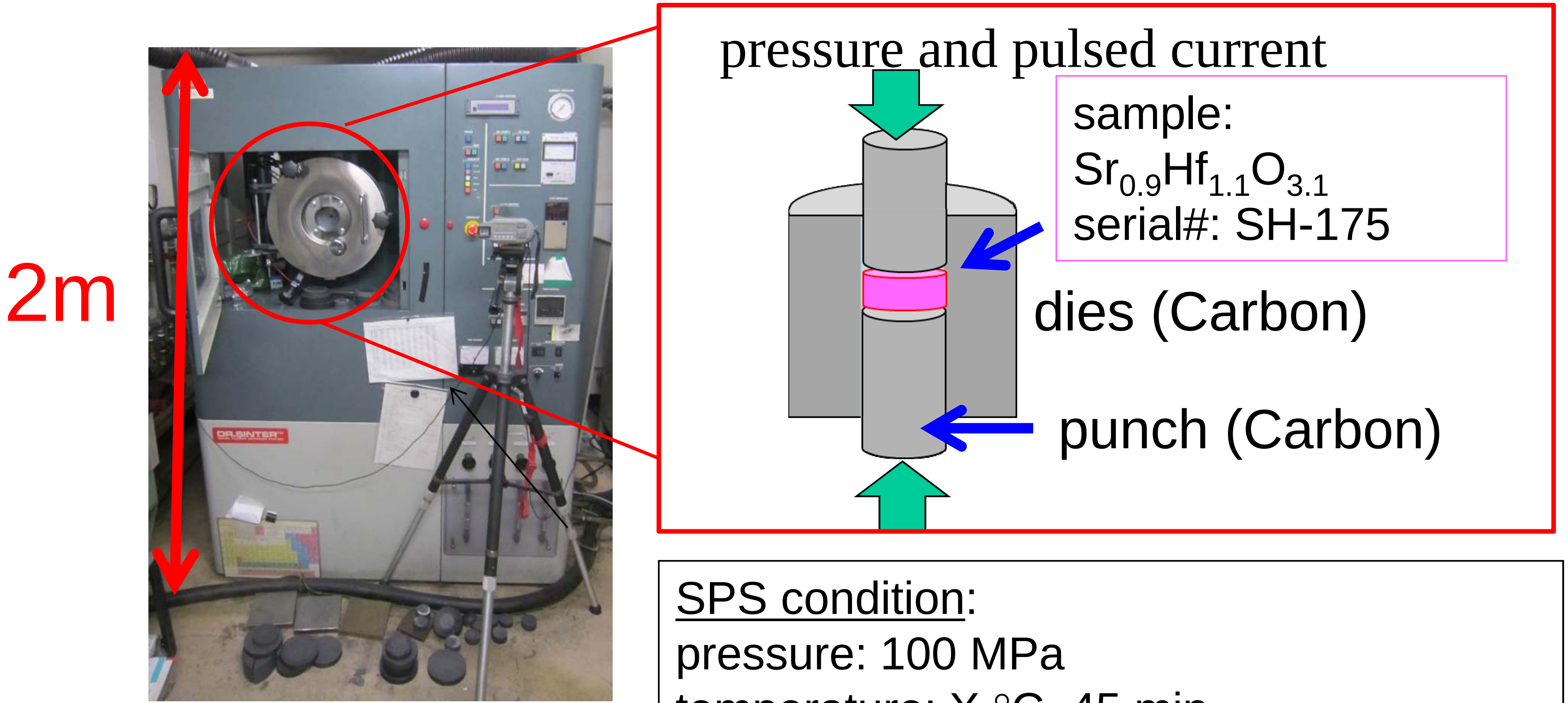


Sr-deficient composition around Sr0.9Hf1.1O3.1 (nSHO) shows an intense and temperature stable (up to 400 K) emission at 335 nm with decay time of about 180 ns at room temperature!

*Nikl et al, Optical Materials **34**, 433 (2011).*

nSHO ceramics prepared by SPS

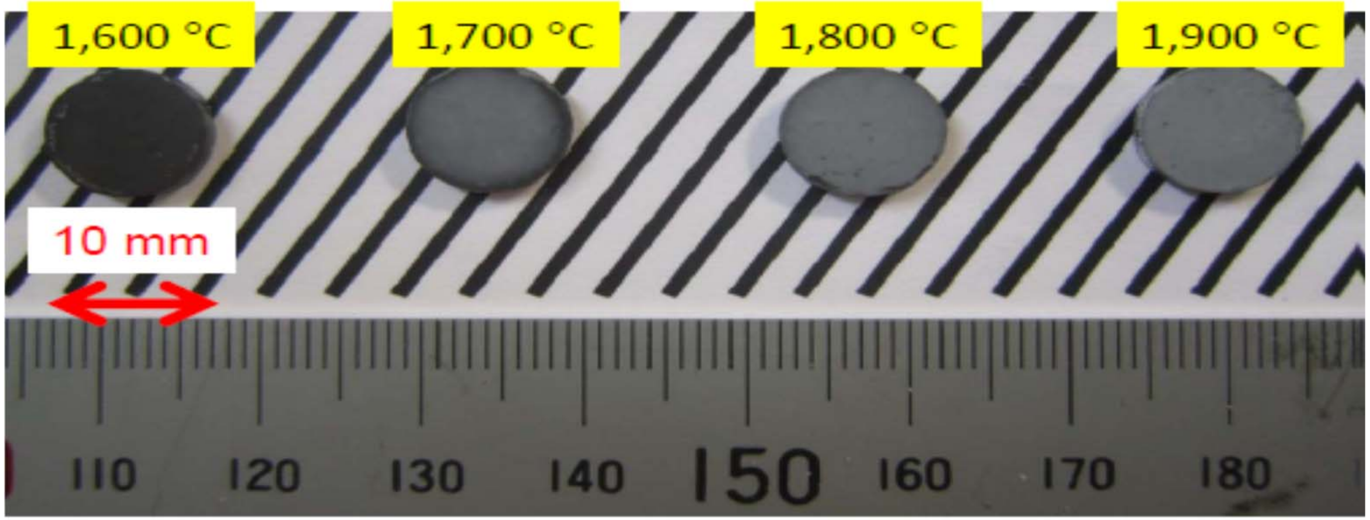
The powder was sintered with DR.SINTER (Fuji Denpa) in Cooperative Research and Development Center for Advanced Materials / IMR.



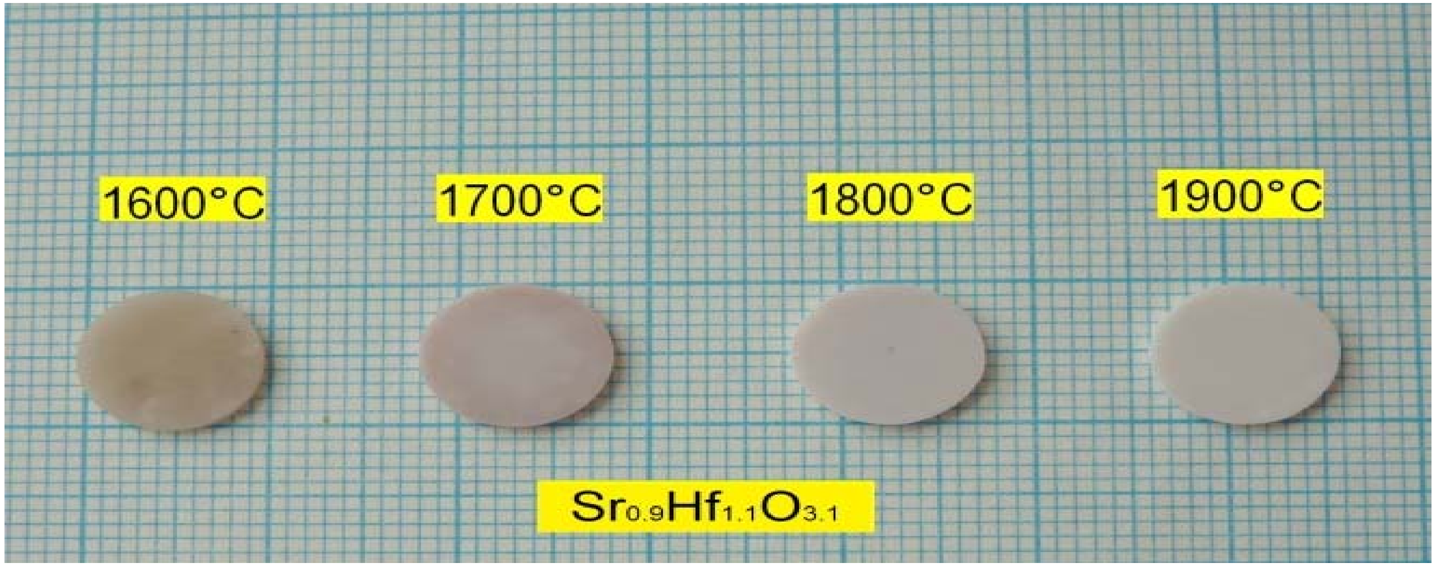
DR.SINTER （Fuji Denpa）

<u>SPS condition</u>:
pressure: 100 MPa
temperature: X °C, 45 min
(x=1,600, 1,700, 1,800, 1,900)
atmosphere: Vacuum (a few Pa)

nSHO ceramics obtained from SPS

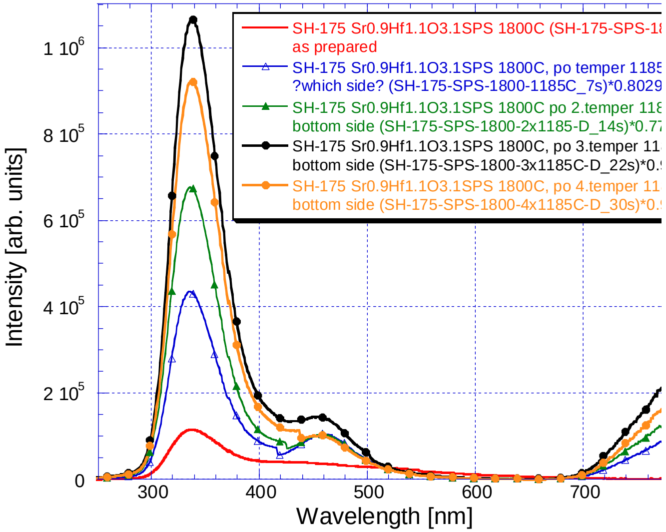


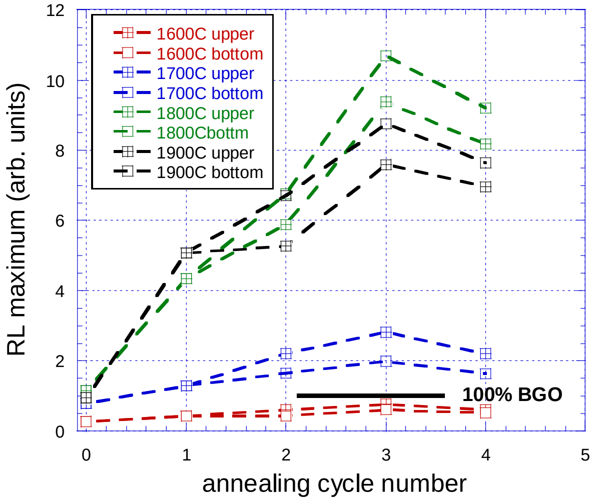
And annealed four times in air 6 hours/ 1185 ^{0}C.

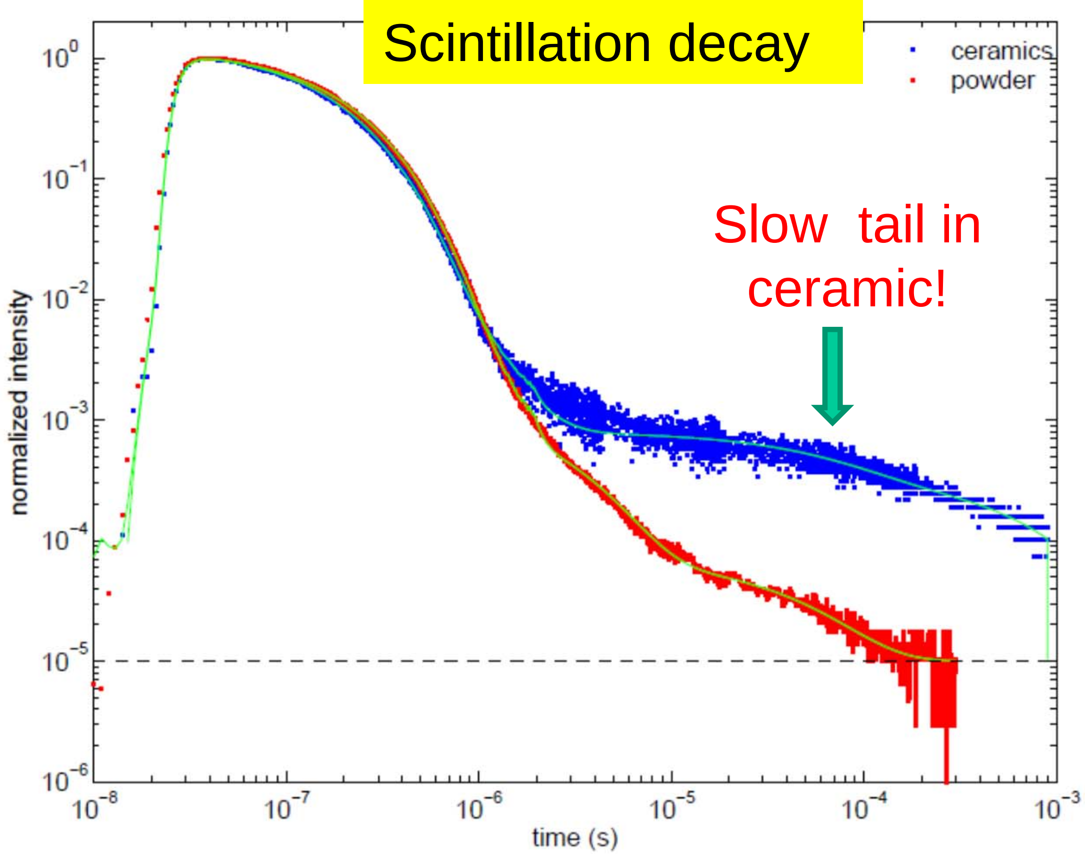


RL and scintillation decay of annealed nSHO ceramics

Radioluminescence spectra







Air annealing-optimized nSHO ceramics exceeds 10x BGO standard in RL intensity, is dominated by PL decay time 180 ns, but shows a slower component at times above 1 us compared to the source powder

Conclusions, perspectives (oxides)

- Sources of energetic radiation and particles are more and more used in different fields of human activity $\Rightarrow$ increasing need for tailored scintillation materials. Recent examples: (i) A^{3+} doped $PbWO_4$

- Invention of new materials (solid solutions interesting) : (i)multicomponent garnets $Gd_3Ga_3Al_2O_{12}$:Ce; (ii) La-admixed pyrosilicate $(Gd,La)_2Si_2O_7$:Ce;(iii) nonstoichiometric $SrHfO_3$

- In Ce-doped orthosilicate and garnet scintillators the role of Ce^{4+} must be revisited. It contributes positively to fast scintillation response by providing new fast radiative recombination pathway. Similar effect is achieved in Eu-doped LiCAF, here we have engineered transition between Eu^{2+} - Eu^{3+} charge states.

- Ce^{4+} can make such a positive job in any oxide scintillator where CT absorption of Ce^{4+} does not overlap with emission spectrum of the material (i.e. not only that of Ce^{3+}, but e.g. also Gd^{3+} and any other one related to the host) . Pr^{4+} is excluded in bulk samples! Annealing in air also helps due to the diminished deep oxygen vacancies-based traps.

- We can monitor hole O^- centers by EPR experiment in garnets, correlation with TSL becomes possible and timing characteristics of Ce^{4+} scintillation cycle can be determined**!**