Specificities of nanoscintillators: processes and applications

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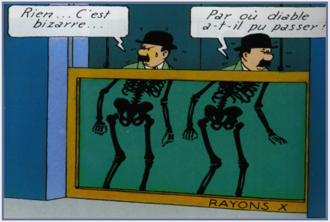
Outline

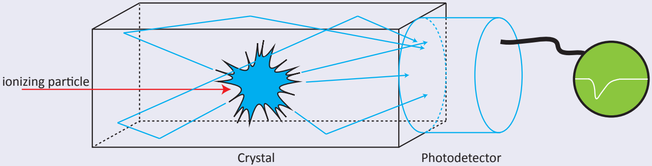
- Introduction
- Application
- Mechanisms

Scintillators in general

Detection of ionizing radiation: Old style

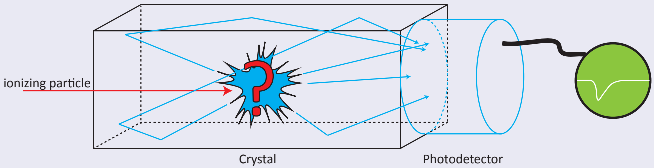


Detection of ionizing radiation: Modern one



About processes

Huge relaxation of Energy



1 high energy photon (keV-MeV) $\rightarrow$ thousands of IR-Vis photons (eV)

About processes

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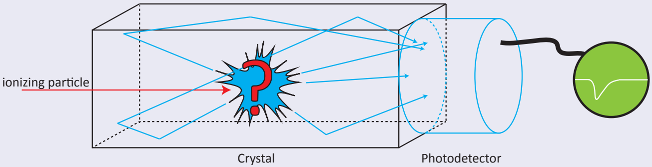


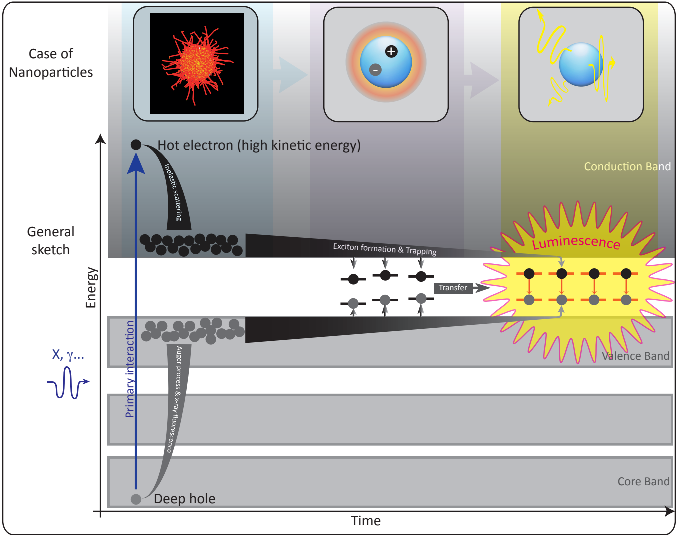
1 high energy photon (keV-MeV) $\rightarrow$ thousands of IR-Vis photons (eV)

Multiscale Physics

- As cutting a 10km string in pieces of a few cm!
- First steps in the ps range, last ones can be in the s time range
- Energy deposition is structured at the nm and mm scale

Scintillation mechanisms

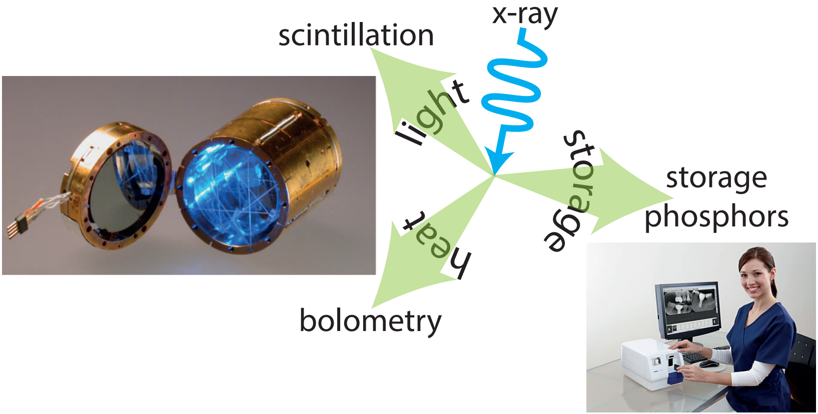
A brief description



Scintillation mechanisms

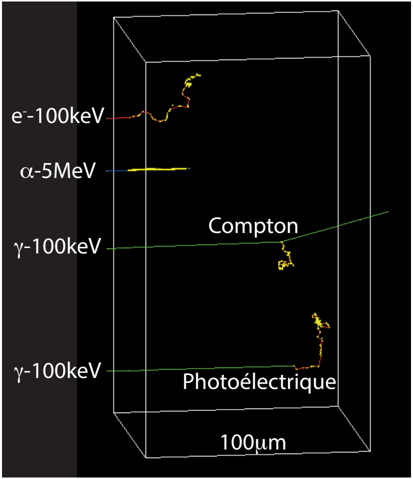
As a result

Energy sharing during the relaxation process → light, heat & storage



Spatial scale?

Simulation with GEANT4 the interaction



example with NaI:Tl

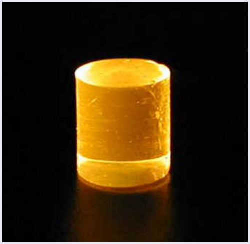
Look at the scale as compared to a nanoparticle of 10 nm diameter!!

Applications

Nanoparticles are small
$\rightarrow$ they can be mixed into host matrix while preserving transparency

In solids

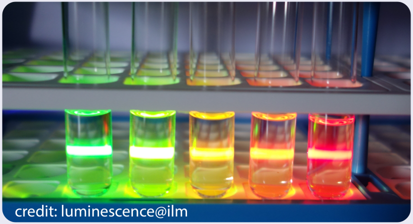
ZnS:Mn NP dispersed in PMMA



http://chm.tu-dresden.de

In liquids

Colloïdal solution of semiconductor nanoparticles



$\rightarrow$ hybrides & liquid scintillators

Applications-Hybrides

Doping with nano particles
Claimed advantages: low cost as compared to single crystals

CdSe/ZnS Qdots in glasses

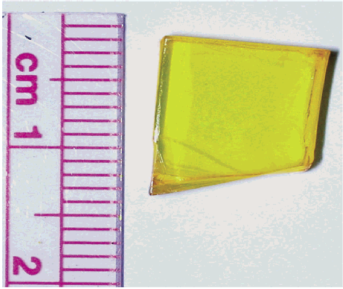
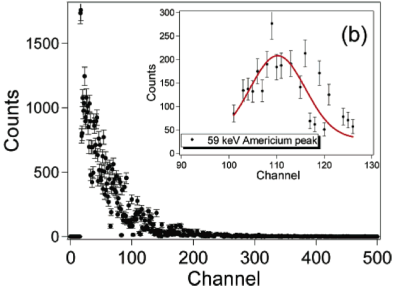


Figure 1. Picture of a 1/16 in. thick nanoporous glass slab impregnated with CdSe/ZnS quantum dots emitting at 510 nm.

Photopeak?

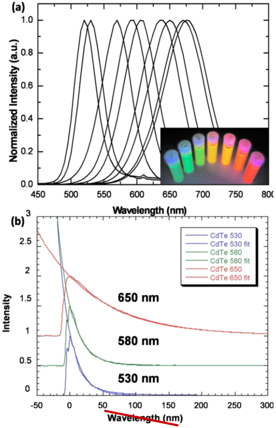


Letant et. al. NanoLetters, 2006

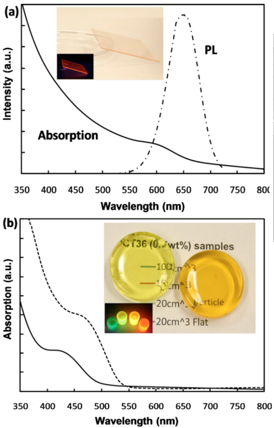
A weak scintillation can be observed

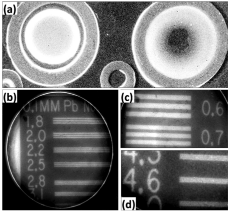
Applications-Hybrides

In the same spirit: CdTe in polymers



decay time (ns)





In conclusion, CdTe QDs and their polymer nanocomposites were studied for x-ray scintillation and imaging applications. The excellent x-ray luminescence results including: high resolution, fast decay, nonafterglow, high stopping power, and superior spectral match to the CCD detector, indicated that CdTe nanocomposite is a promising nanophosphor candidate for x-ray imaging applications.

Kang et. al. Appl. Phys. Lett 2011

Probably a bit optimistic ...

Applications-Hybrides

In the same spirit, but with $LaF_3 : Ce^{3+}$ but in organics

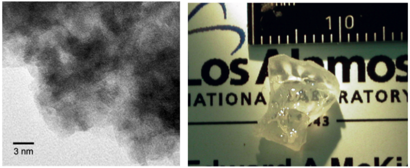
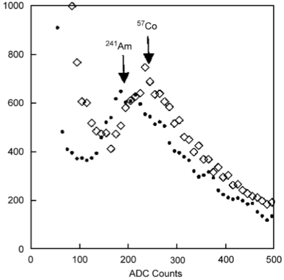


Figure 1. Transmission electron microscopy image of the Ce:LaF$_3$ particles (left) and a 1cm thick oleic-based nancomposite of Ce:LaF$_3$ with nearly 30% volume loading of the phosphor.



McKigney et. al., NIMA, 2007

issue → high loading while preserving the transparency & properties

personal opinion :
not sure that it can compete with crystals regarding performances.

Application-Hybride

US Congres report

Congressional Research Service

Detection of Nuclear Weapons and Materials: Science, Technologies, Observations

Jonathan Medalia
Specialist in Nuclear Weapons Policy

June 4, 2010

...However, unexpected nanoscale physics could impair energy resolution...

Application-Hybride

Doping organics with optically "active" nano particles specific functionality: neutron detection/ increase of density

Radiation Measurements 48 (2013) 7–11

Contents lists available at SciVerse ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

GdBr$_3$:Ce in glass matrix as nuclear spectroscopy detector

Z.T. Kang, R. Rosson*, B. Barta, C. Han, J.H. Nadler, M. Dorn, B. Wagner, B. Kahn

Georgia Tech Research Institute, Georgia Institute of Technology, 925 Dalney St NW, Atlanta, GA 30332, USA

Fig. 1. Cerium-activated gadolinium bromide glass-matrix cylinder, 2.5-cm dia. × 3.0-cm height, under 365 nm UV illumination.

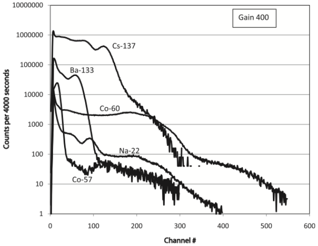


Fig. 3. Five gamma-ray spectra with 2.5-cm dia., 3.0-cm height, alumina-silica glass-matrix detector at gain 400.

Some attempts to use NanoParticles

Doping organics with optically "passive" nano particles
Gd_2O_3 in organic scintillator

→ neutron detection?

Cai et. al., J. of. Mat. Chem. C, 2013

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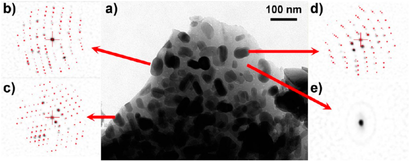
Cai et. al., J. of. Mat. Chem. C, 2013

NP in silica at a tip of an optical fiber
potential use for dosimetry during radiotherapy



Baraldi et. al., J.Phys.Chem. C, 2013
& A. Vedda's group works

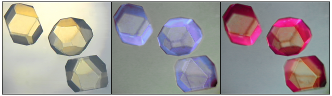
Application-New Materials

Alternative materials: MOF
A way to embed metal in organic without any quenching

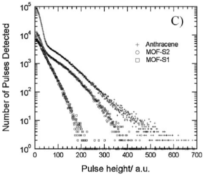
www.advmat.de ADVANCED MATERIALS

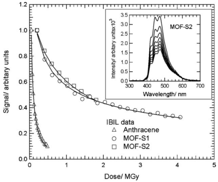
Scintillating Metal-Organic Frameworks: A New Class of Radiation Detection Materials

By *F. P. Doty,* C. A. Bauer, A. J. Skulan, P. G. Grant,* and *M. D. Allendorf**



https://share.sandia.gov



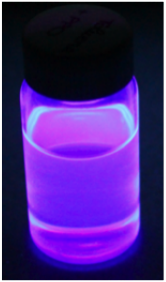


Not really nano, but a competitor

Application-Liquid Scintillation

Various potential applications: metrology, neutrino

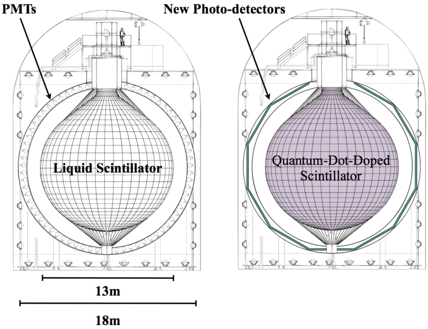
Toluene + PPO molecule

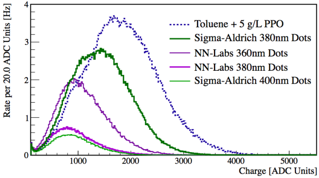


- molecule $\leftrightarrow$ active nanoparticles?
- Advantage: a larger Stokes shift
- Drawbacks: stabilization of high concentration & knowledge about energy transfers?

Application-Liquid Scintillation

One example: ^{113}Cd high neutron cross-section with γ cascade of 9MeV
$\rightarrow$ Antineutrino measurement
^{116}Cd : double β decay candidate





Winslow et. al., JINST, 2012

In this case the Stokes shift is not so large, cost???

Other applications see session 3 on monday:
polymers, fast detectors, ESQUIRE project...

Nanoscintillator for Photodynamic therapy

Photodynamic effect: cytotoxic effect induced by light activation of a molecule - photosensitizer

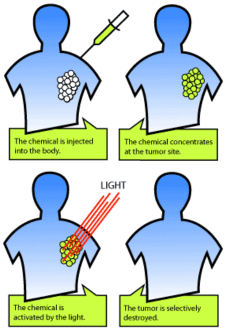


Figure from Modern Cancer Hospital Guangzhou

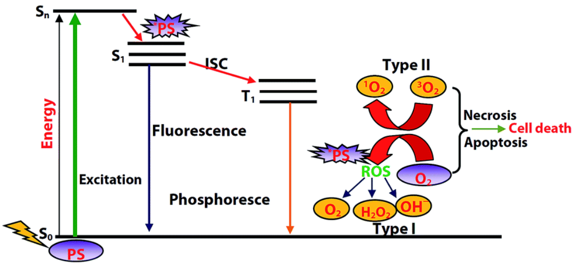
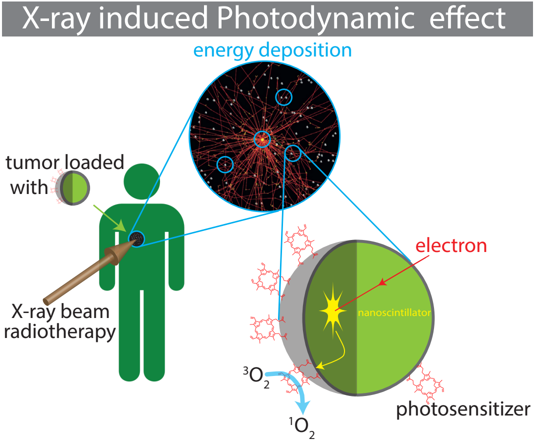


Figure from Majumdar et. al. J.Phys.Chem.C, 2014

→ Due to the penetration depth of light in tissues, the PDT is limited to the treatment of tumors localized on surface (or through endoscopy)

About Photodynamic Therapy under x-rays

Using Nanoscintillators as internal light sources
(Biblio: Chen, J.NanoSc. Nanotech. 2006, Liu-APL-2008, Juzenas-Adv.Drug.Delivery-2008)

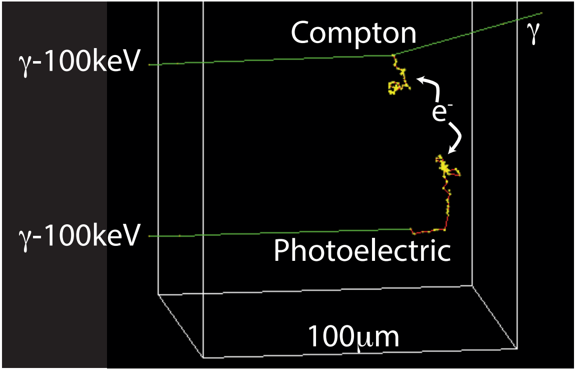


See next talk from Dr. Anne-Laure Bulin

Changes on the energy distribution

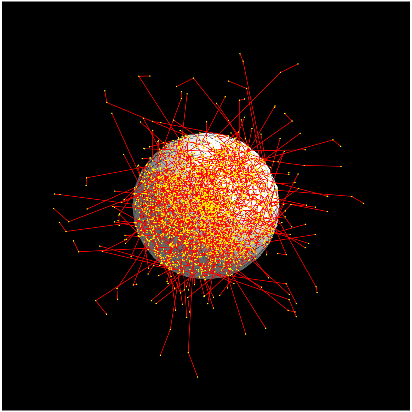
The mean free path of charges during the energy relaxation is $\gg$ than the particle size

MonteCarlo simulated photoelectric and Compton events in NaI

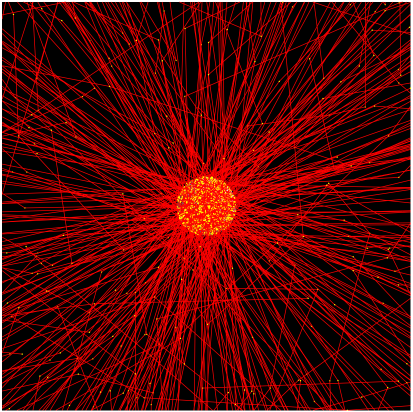


Changes on the energy distribution

1keV electron in the NP (Gd_2O_3)



10keV electron in the NP (Gd_2O_3)



→ A significant fraction of the energy is deposited out of the particle.

Changes on the energy distribution

More details in

ROYAL SOCIETY OF CHEMISTRY

Nanoscale

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Cite this: DOI: 10.1039/c4nr07444k

Modelling energy deposition in nanoscintillators to predict the efficiency of the X-ray-induced photodynamic effect†

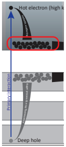
Anne-Laure Bulin,[a] Andrey Vasil'ev,[b] Andrei Belsky,[a] David Amans,[a] Gilles Ledoux[a] and Christophe Dujardin*[a]

→ less that 1% of the energy is deposited in the NPs in case of diluted samples and out of potential back transfer to the NPs

See next talk from Dr. Anne-Laure Bulin

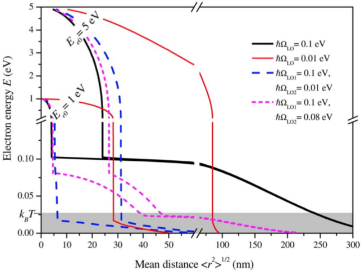
Thermalization and nanosizes

The situation is even worse when considering thermalization



Interaction with Phonons

Thermalization length $\gg$ particle size



Kirkin et al. IEEE-TNS 2012

See my talk on Monday morning

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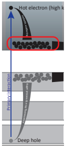

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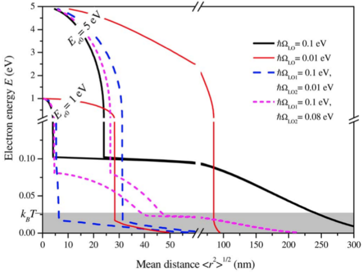

Kirkin et al. IEEE-TNS 2012

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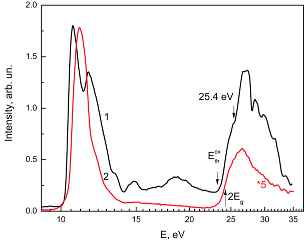
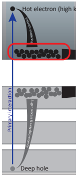
STE emission of 20nm and 140nm CaF_2 particles
$\rightarrow$ effect of thermalization length



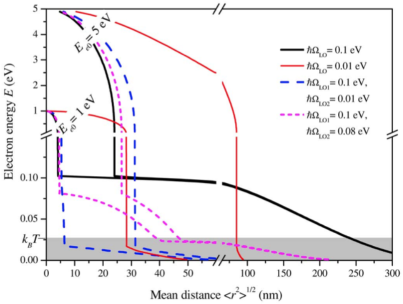
Vistovskyy et. al., J. of Applied Phys., 2012

role of the thermalization



Interaction with Phonons

Thermalization length ≫ particle size



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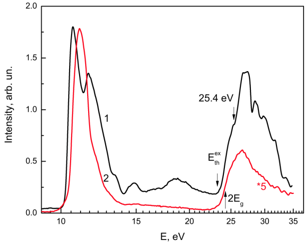
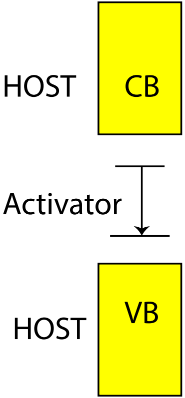


Vistovskyy et. al., J. of Applied Phys., 2012

Doped insulators and semi-conductors

I need to introduce these two classed of materials

Doped insulators



Activator emission: localized

Doped insulators and semi-conductors

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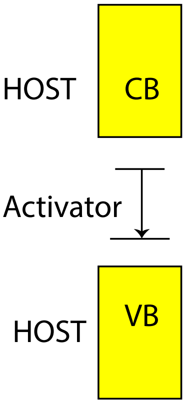
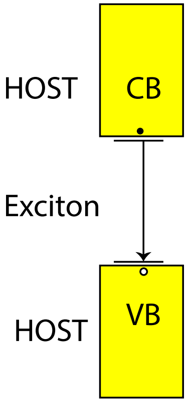
Doped insulators



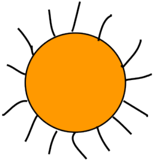
Semi-Conductors

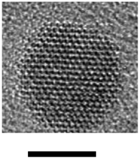


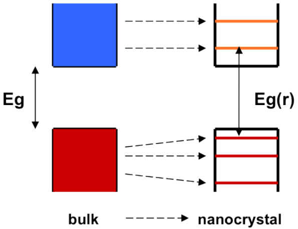
Activator emission: localized

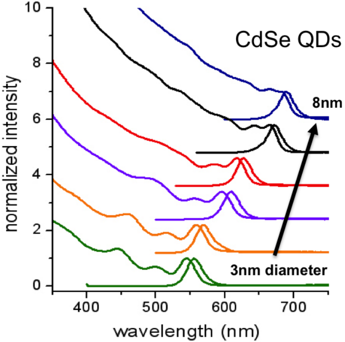
Excitonic emission: non-localized

Q-Dots are confined semi-conductors (See J.Houel's talk)



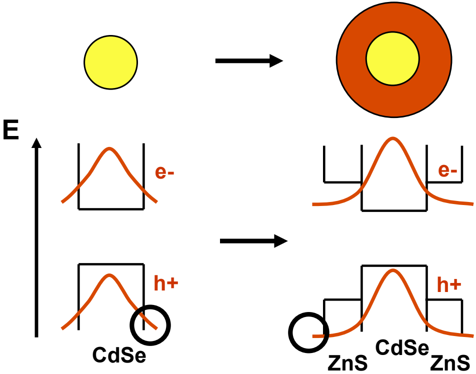






Core/Shell structures

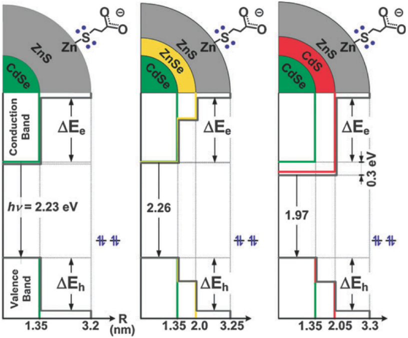
- Generally capped to improve the luminescence efficiency (traps are pushed away from the active core)
- The shell thickness modifies the confinement
- The nature of the shell modifies the confinement
- It plays as well on the localization of the charges



New Physics: $\beta.S.Q$

Potential barrier for low energy electrons

Nanotechnologies use to play with potential barriers and Gap



Bonghwan Chon, PhysChem.ChemPhys, 2009

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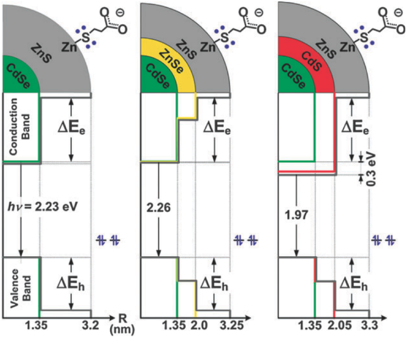
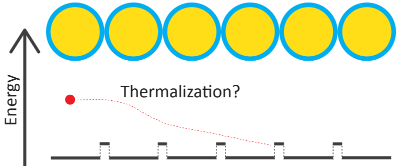


Bonghwan Chon, PhysChem.ChemPhys, 2009

Assembly of core-shell system might create structured potentials



Effect on spacial distribution of charges during relaxation → non-proportionnality?

Role of the charging effect?

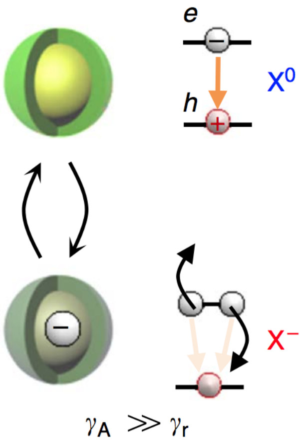
Excitons in semi conductors Q-dots

- As for low energy electrons and holes, excitons have a mobility $\rightarrow$ effect on the rise time in case of transfer to activator? $\rightarrow$ potential barrier at the particle edge?

Role of the charging effect?

Excitons in semi conductors Q-dots

- As for low energy electrons and holes, excitons have a mobility $\rightarrow$ effect on the rise time in case of transfer to activator? $\rightarrow$ potential barrier at the particle edge?
- Charging effect $\rightarrow$ Auger process instead of radiative recombination



Galland et. al., Nature Comm., 2012

More details during my talk (monday morning)

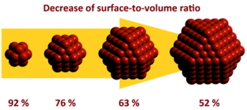
New Physics: $\beta.S.Q$

Traps (see A.Vedda's talk for more details)

Traps might be different in nanoparticles

Stress

Large Surface/Volume ratio



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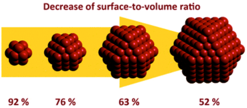
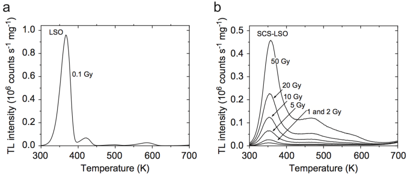
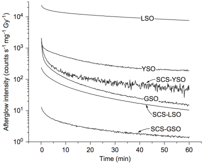
Stress

Large Surface/Volume ratio



Exemple with LSO (25-100nm) as precursor for ceramics





Yukihara, J.of.Lum, 2010

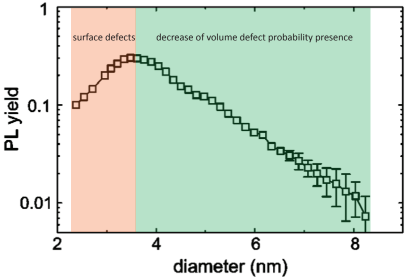
Effect on afterglow, Bright Burn / might be good for Photostimulation applications

New Physics: $\beta.S.Q$

Traps: example with Silicon

- Indirect band gap → the yield is driven by the defect concentration
- at small sizes, the probability to find a bulk defect is smaller
- at very small sizes, surface defects → requires surface passivation

Evolution of the Light Yield with the size



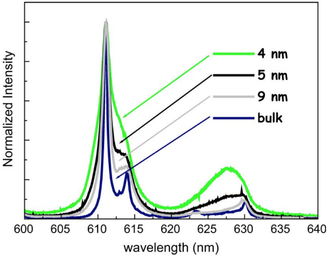
Ledoux, Applied Phys. Let., 2002

New Physics: $\beta.S.Q$

Effects on Luminescence

Disorder $\rightarrow$ Broadening

Case of nano-Gd_2O_3 : Eu^{3+}



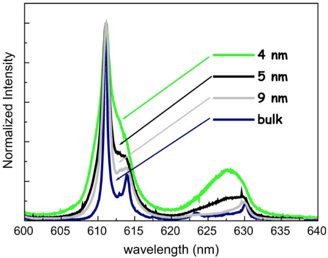
Dujardin et. al., IEEE TNS, 2010

New Physics: $\beta.S.Q$

Effects on Luminescence

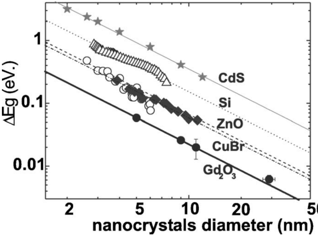
Disorder → Broadening

Case of nano-$Gd_2O_3 : Eu^{3+}$



Dujardin et. al., IEEE TNS, 2010

Ionic materials ∼ flat bands
→ No confinement effect on gap

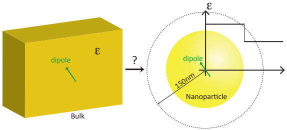


Mercier et. al., J.Chem. Phys., 2007

New Physics: $\beta.S.Q$

Effects on Luminescence: Dielectric confinement

The radiative decay time depends on the index of refraction which is a macroscopic parameter

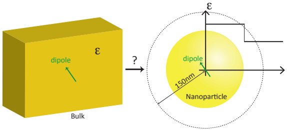


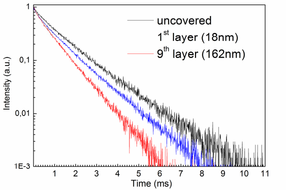
New Physics: $\beta.S.Q$

Effects on Luminescence: Dielectric confinement

several models: Fully macroscopics, empty and virtual cavity

The radiative decay time depends on the index of refraction which is a macroscopic parameter





LeBihan et. al., PRB, 2008

→ nano-LuAG:Ce $\tau =$ 117ns vs 58ns in bulk
(Barta et.al. J.Mat.Chem,2012)

In addition, competition between radiative and non-radiative probabilities

Take care

"Nano-things" are not always fantastic

Here normalization by the mass !!!

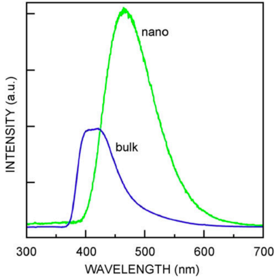


Fig. 2. Radioluminescence of bulk and nano YSO:Ce as a function of wavelength. Light output is normalized to the mass of the sample.

4. Conclusions

An alternative to material discovery for the improvement of scintillator performance has been presented. By exploiting the effects of reduced particle size, improved scintillators can be created. Three different effects that would be expected to produce increased light output in the nanocomposite, as compared to the bulk, have been experimentally observed.

McKigney NIM-A 2007

A lot of phenomena interplays, and it is not so easy to extract tendencies...