Scintillators

Basics and Practical Aspects

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INSIS
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What we will cover

- Brief History
- Practical Properties
- Organic Scintillators
- Inorganic Scintillators
- Neutron Scintillator Examples
- Practical Implications in Neutron Detectors

Radiation and Scintillation

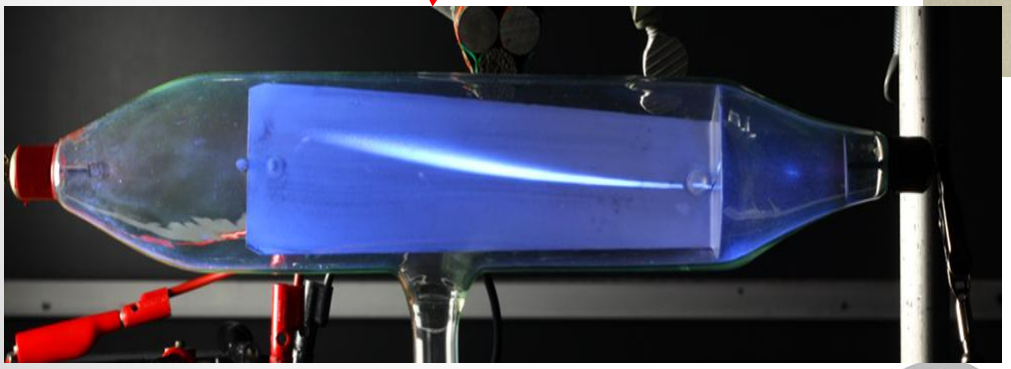
The Beginning

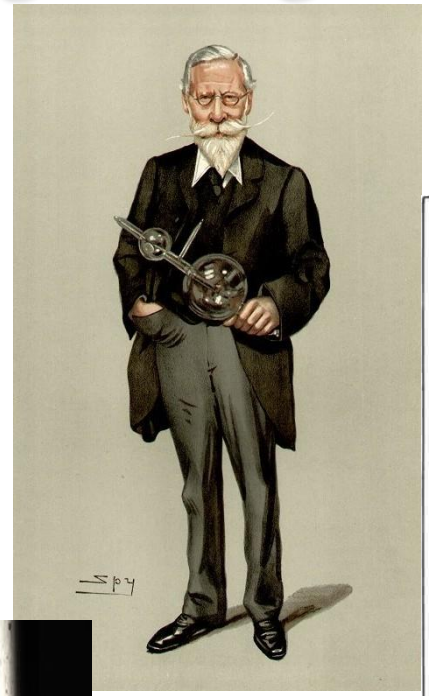
- $CaWO_4$ & ZnS

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.





The Power of Radium at Your Disposal

Twenty-three years ago radium was unknown. Today, thanks to constant laboratory work, the power of this most unusual of elements is at your disposal. Through the medium of Undark, radium serves you safely and surely.

Does Undark really contain radium? Most assuredly. It is radium, combined in exactly the proper manner with zinc sulphide, which gives Undark its ability to shine *continuously* in the dark.

Manufacturers have been quick to recognize the value of Undark. They apply it to the dials of watches and clocks, to electric push buttons, to the buckles of bed room slippers, to house numbers, flashlights, compasses, gasoline gauges, autometers and many other articles which you frequently wish to see in the dark.

The next time you fumble for a lighting switch, bark your shins on furniture, wonder vainly what time it is *because of the dark*—remember Undark. *It shines in the dark.* Dealers can supply you with Undarked articles.

For interesting little folder telling of the production of radium and the uses of Undark address

RADIUM LUMINOUS MATERIAL CORPORATION
99 PINE STREET - - - - - NEW YORK CITY
Factories: Orange, N. J. Mines: Colorado and Utah

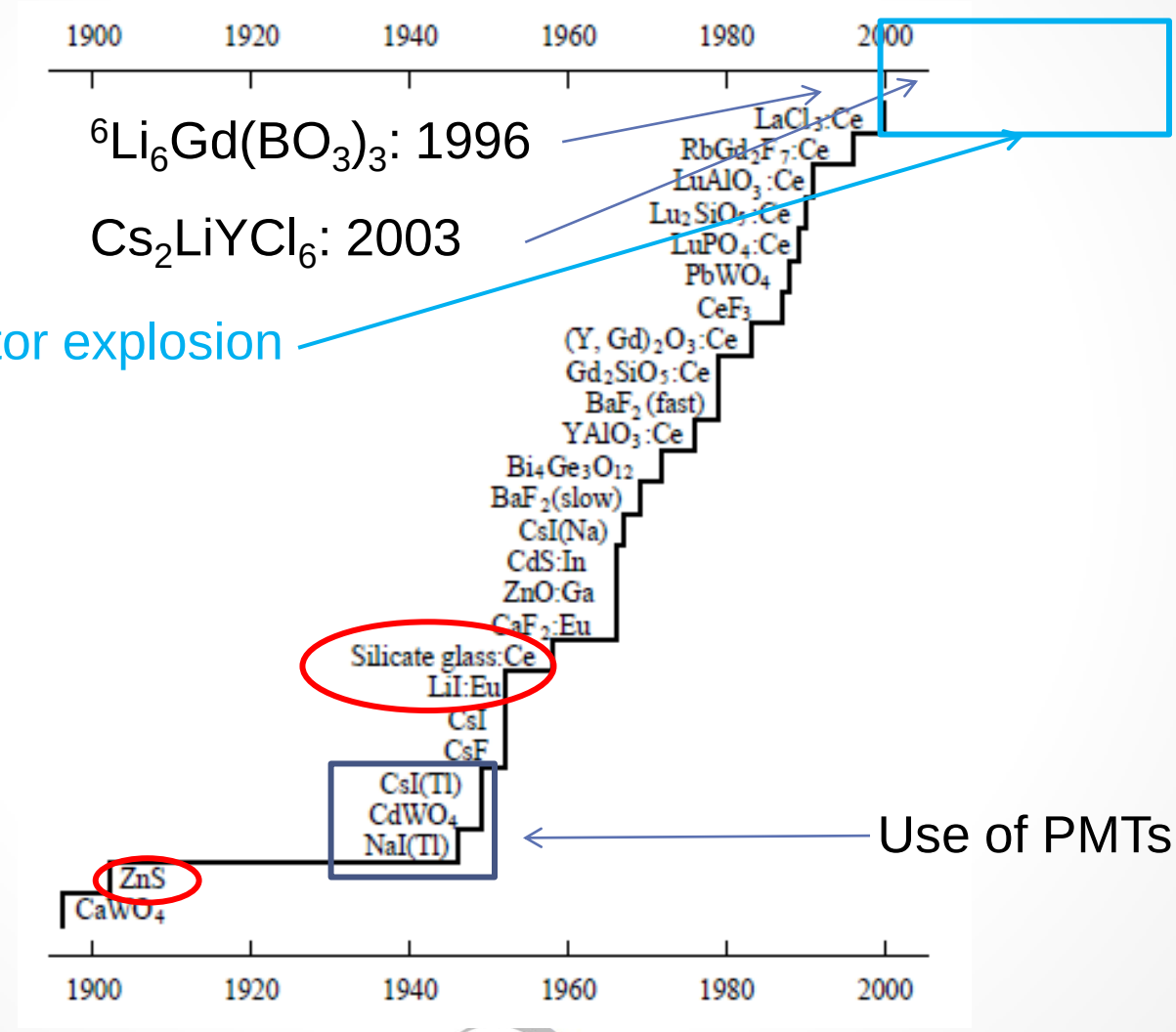
To Manufacturers

The number of manufactured articles to which Undark will add increased usefulness is manifold. From a sales standpoint, it has many obvious advantages. We gladly answer inquiries from manufacturers and, when it seems advisable, will carry on experimental work for them. Undark may be applied either at your plant, or at our own.

The application of Undark is simple. It is furnished as a powder, which is mixed with an adhesive. The paste thus formed is painted on with a brush. It adheres firmly to any surface.

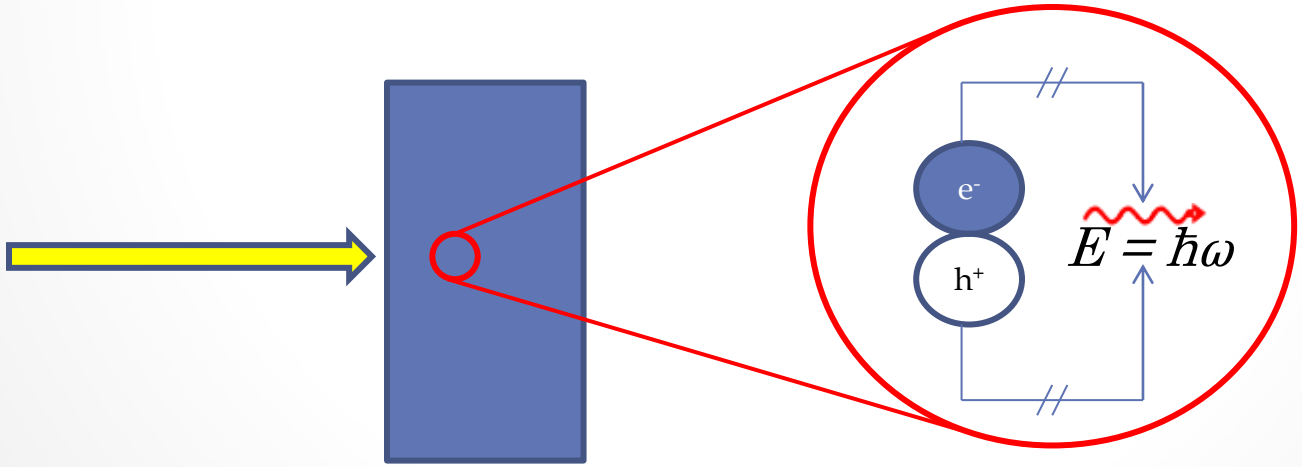
UNDARK
Radium Luminous Material
Shines in the Dark

(Inorganic) Scintillator Timeline

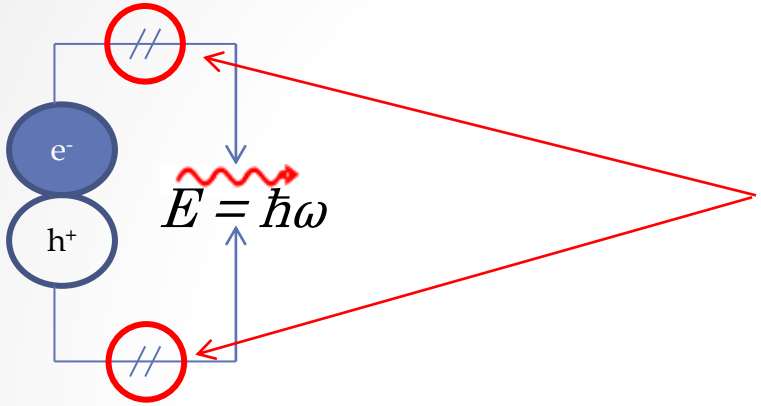


Luminescence

- Chemi-luminescence
- Cathodo-luminescence
- Thermo-luminescence
- Photo-luminescence
- Radio-luminescence (Scintillation)



Scintillators in General



Dictated by physical properties of the scintillator which determines scintillation properties

- Organic Scintillators – determined by Benzene ring
  - Crystalline, Plastic, Liquid, Gas
- Inorganic Scintillators – determined by material (usually crystal) structure
  - Crystal, Glass, Ceramics
  - Most common scintillators for neutron scattering detectors

What are some important properties of scintillators for neutron detection?

- Light yield (typically in photons/MeV for gamma or photons/neutron)
  - Scintillation efficiency
- Emission (and absorption) spectra
  - Need to be able to detect light
- Decay time
  - Count rate capability and n/γ pulse shape discrimination
- α/β ratio
  - n/γ discrimination
- Density and atomic number (ρZ^4_{eff})
  - n/γ discrimination
- Hygroscopicity

Aside on Efficiencies

- Scintillation efficiency and neutron detection efficiency are not the same things!
- Scintillation efficiency $\eta = \frac{energy\ of\ scintillation\ light}{enrgy\ deposit} = \frac{h\nu_e}{w_{e-h}} T q_A$

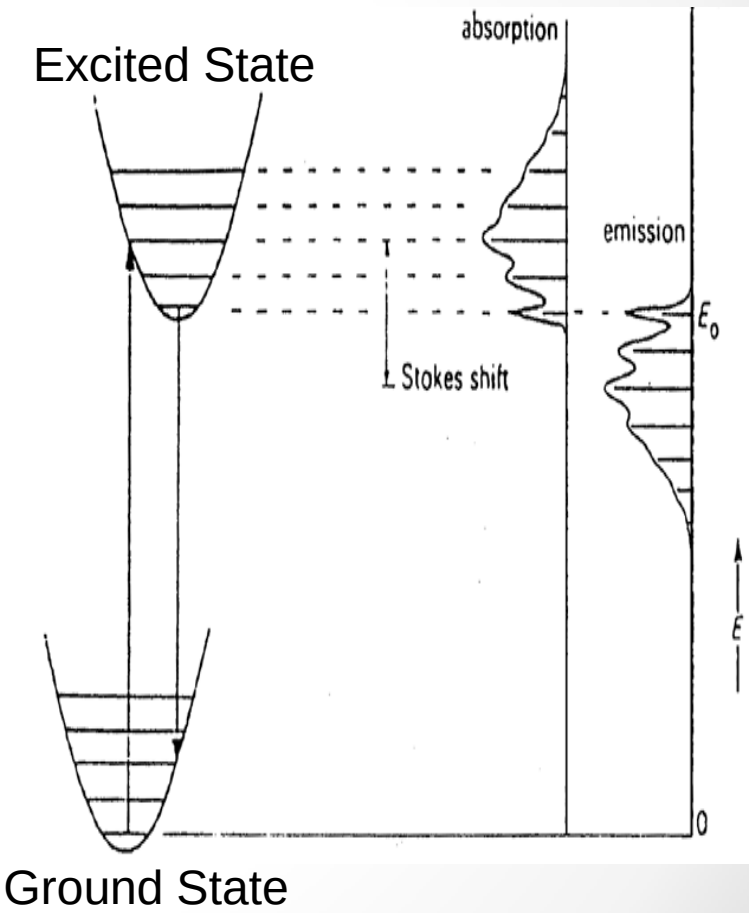
  $h\nu_e$ = average energy of emitted photon
  w_{e-h}=energy required to create one electron-hole pair,
  T=energy transfer efficiency from excited ion to luminescence centre
  q_A= quantum efficiency of luminescence centre

- Estimate maximum efficiency by setting T and $q_A = 1$
- Neutron detection efficiency: $\varepsilon = 1 - e^{-N\sigma t}$

  σ = absorption cross-section
  N = number density of absorber
  t = thickness

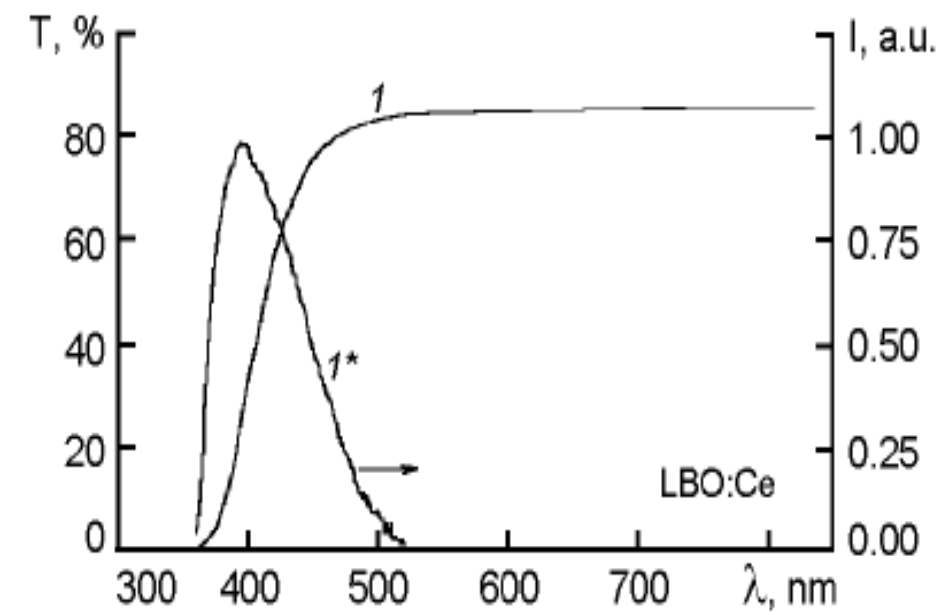
Emission and Absorption

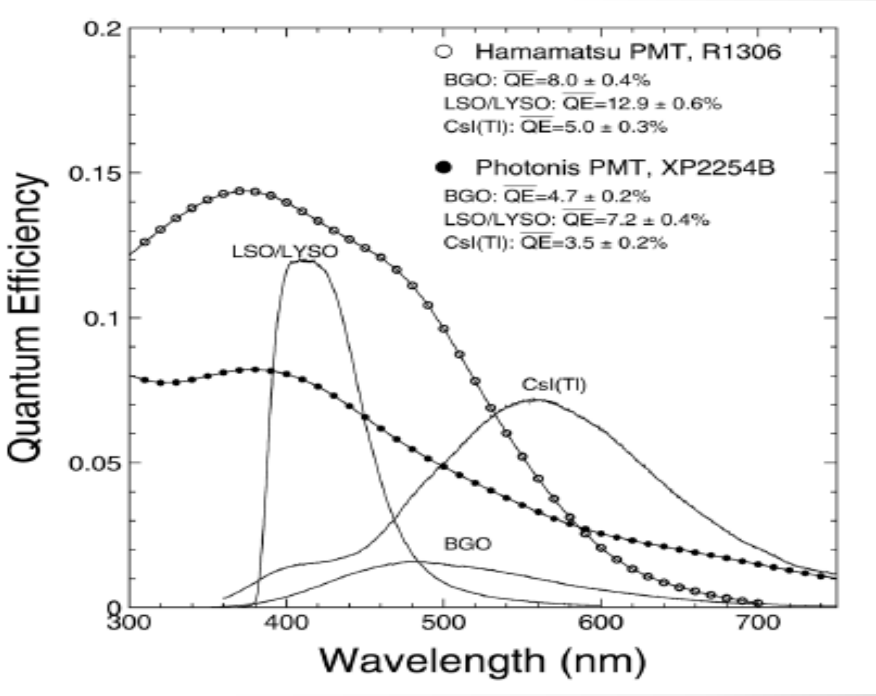
- Light is emitted as a result of radiative transition from an excited state to ground state
- All scintillators emit light at less energy than they absorb (Stokes shift)
  - The process that dictates the Stokes shift is different in different scintillators
  - The larger the Stokes shift, the more transparent the scintillator is to its own emission



How do these properties relate to real world neutron detection?

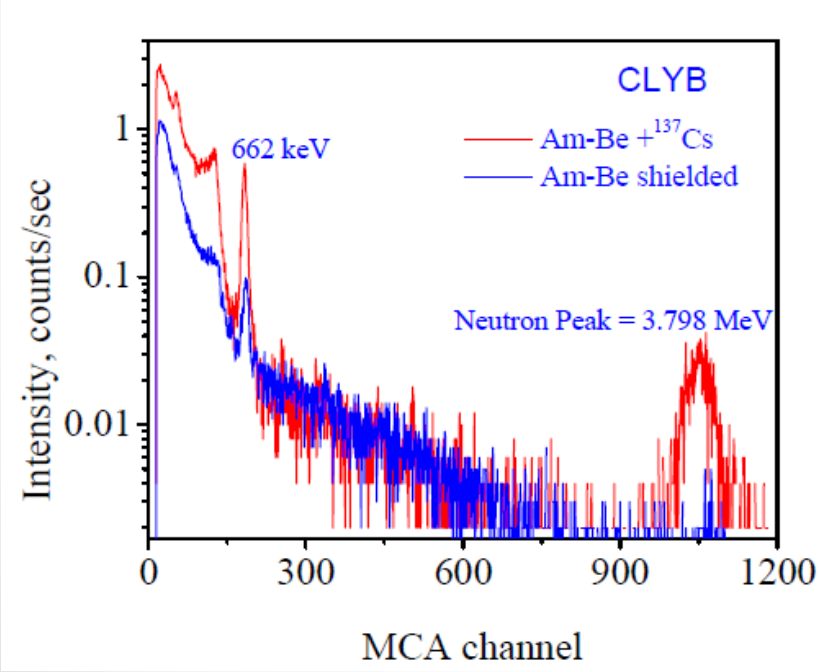
- The scintillator needs to transmit its own light
- Emission spectra needs to match QE of the light detector (PMT, SiPM, PD...) and/or readout mechanism

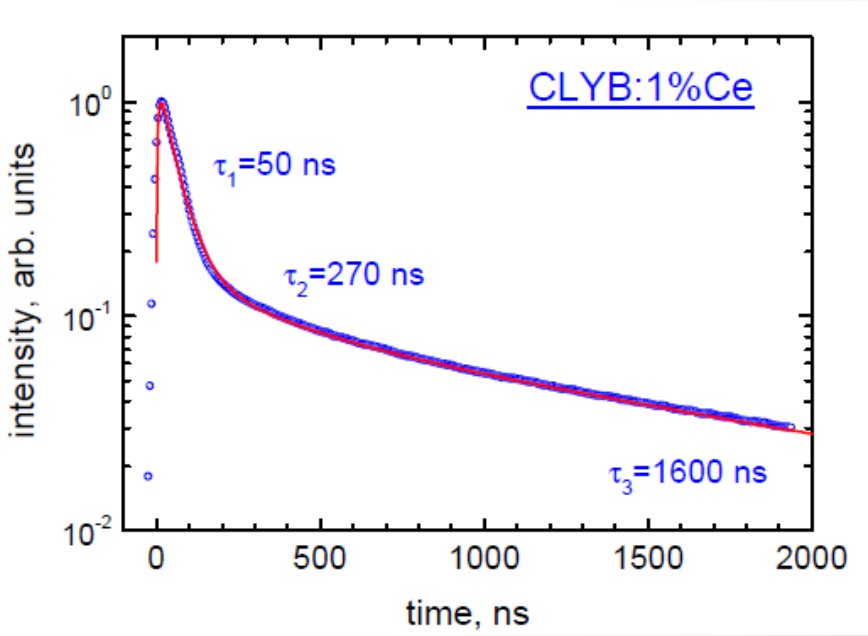




How do these properties relate to real world neutron detection?

- Light yield and α/β ratio: Pulse height spectra
- Decay time: Pulse shape and Count rate

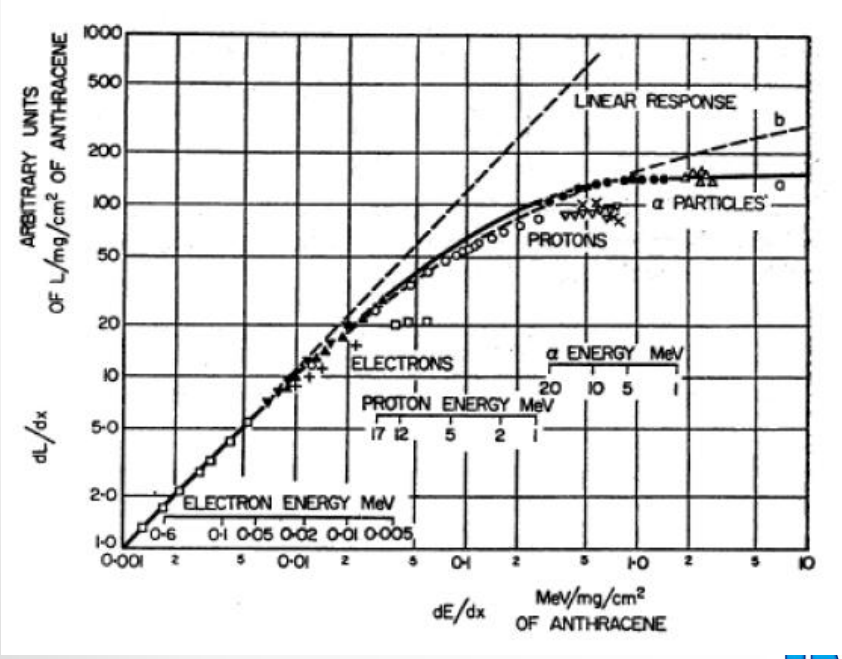


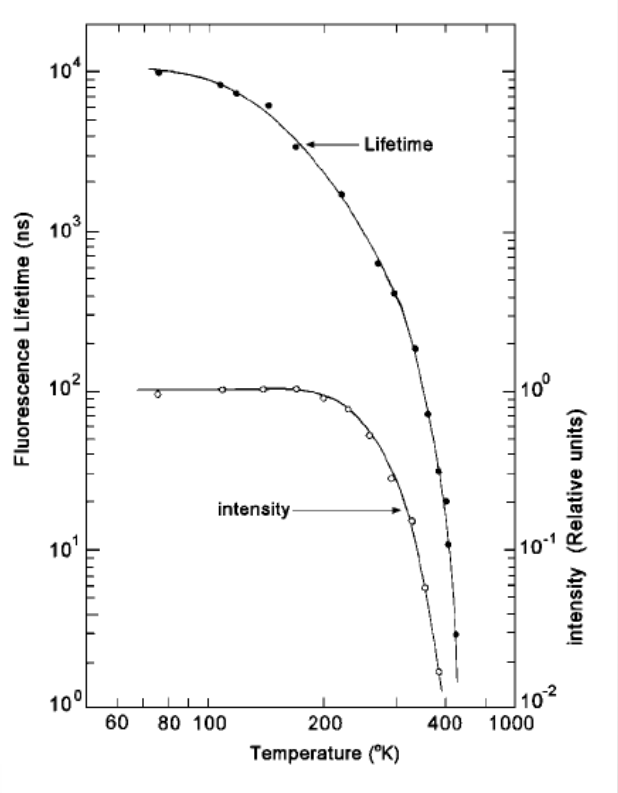


Shirwadkar, U. et al, Investigating Scintillation Properties of Ce Doped Cs2LiYBr6.

Light Yield - Quenching

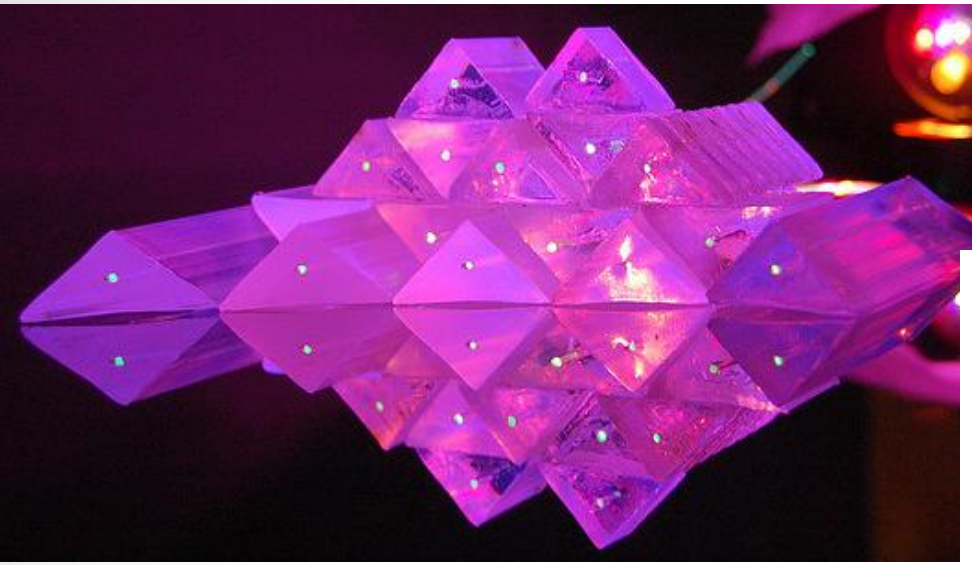
- Reduction in light yield of a scintillator's ideal response is called quenching
- Many different quenching mechanisms
  - Ionization density – responsible for α/β ratio
  - Impurities (i.e. storage phosphors)
  - Thermal

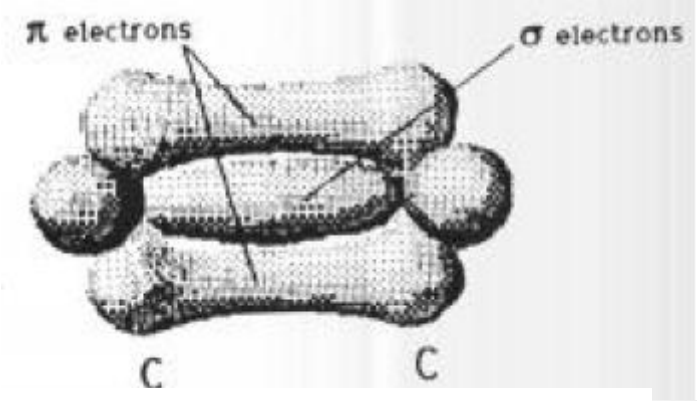


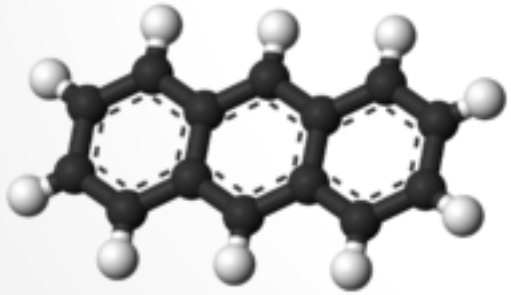


Organic Scintillators

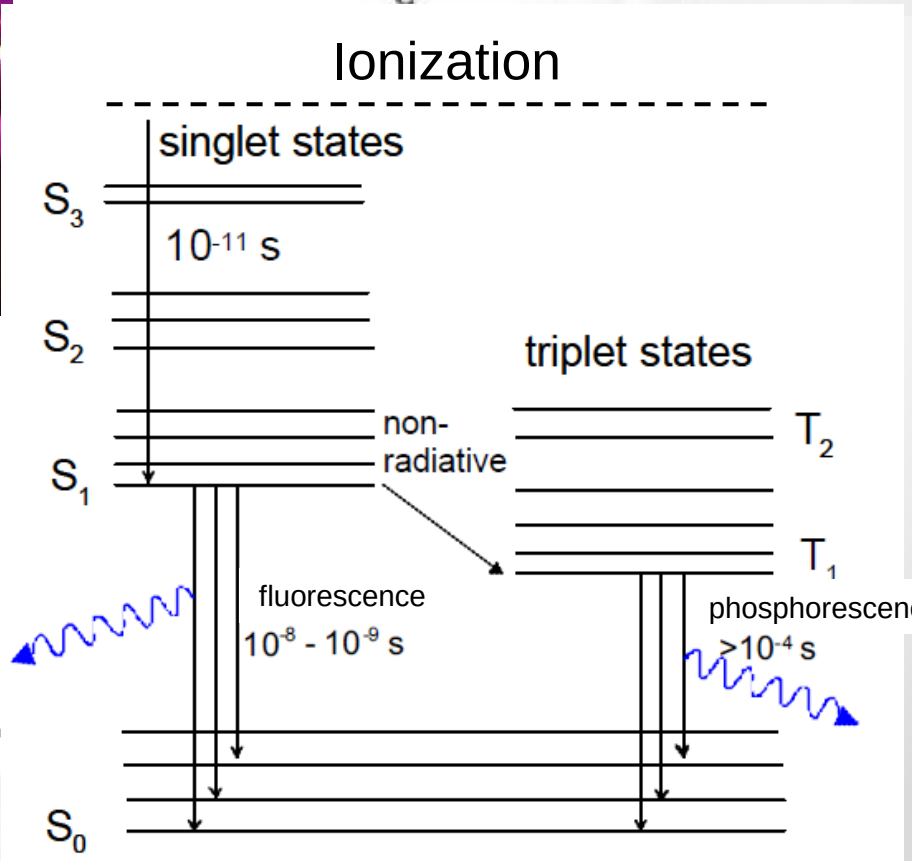
Crystalline





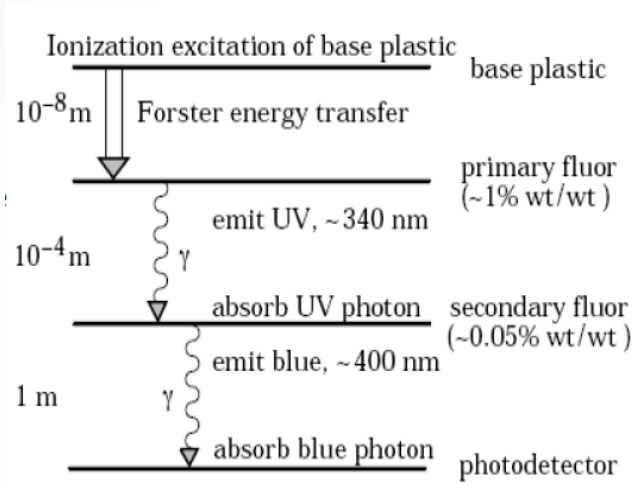


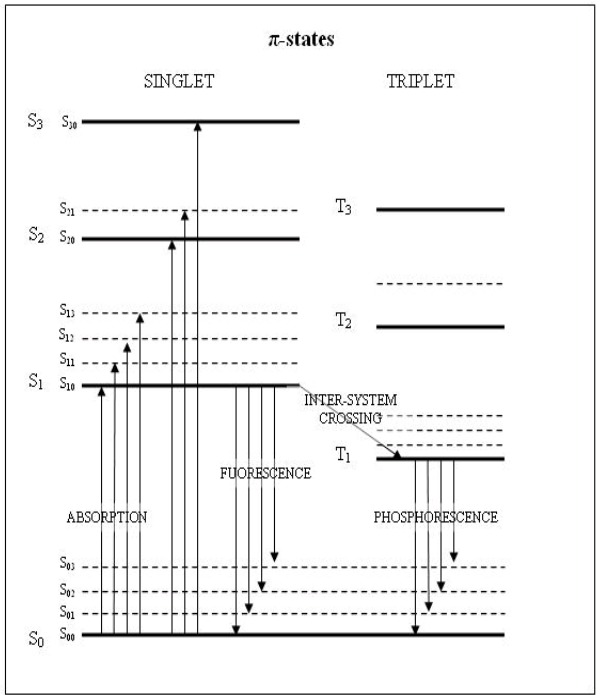
Example: Anthracene



Organic Scintillators

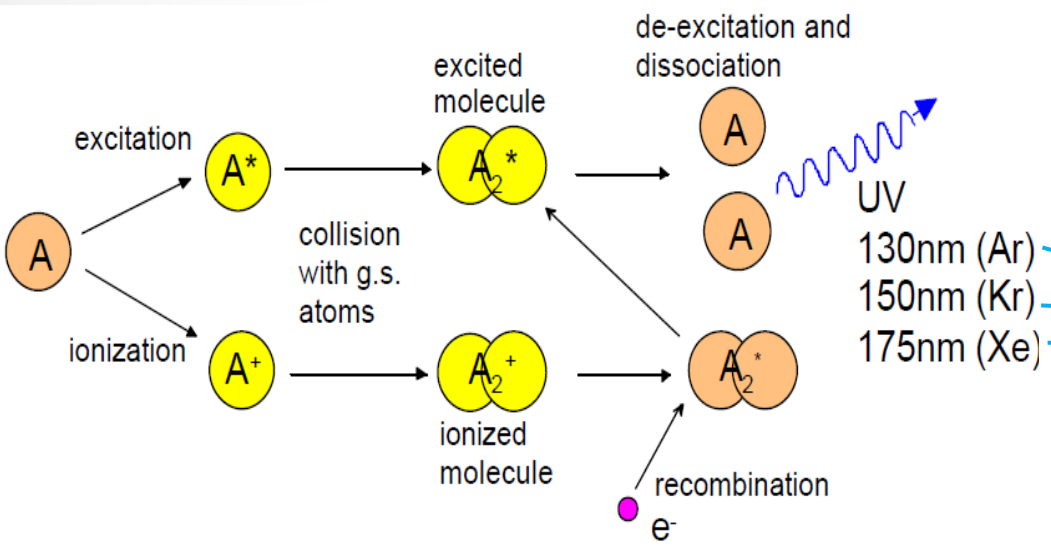
Plastics and Liquids

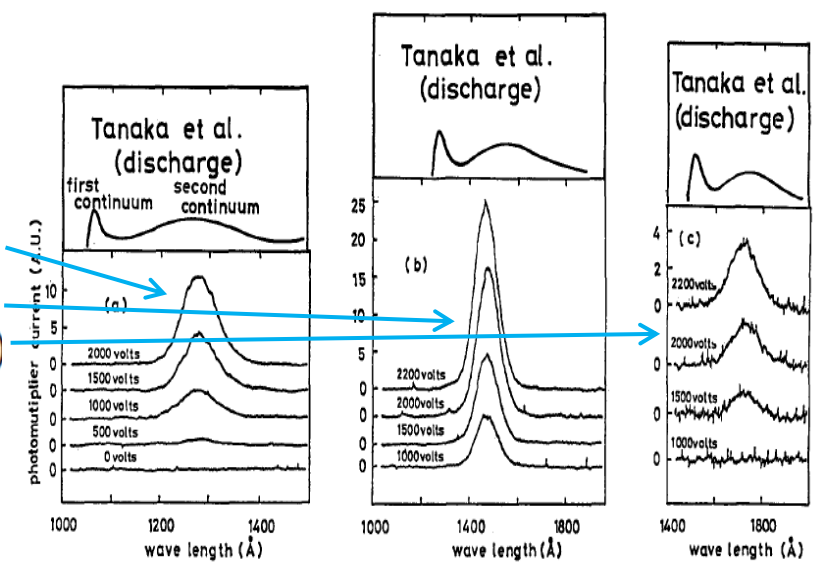




Noble Gas Scintillation

- Excited atoms form dimers in either singlet or triplet state
- 2 time constants observed ~10^{-9} s and ~10^{-7}-10^{-6} s
- Used in Gas Scintillation Proportional Counters

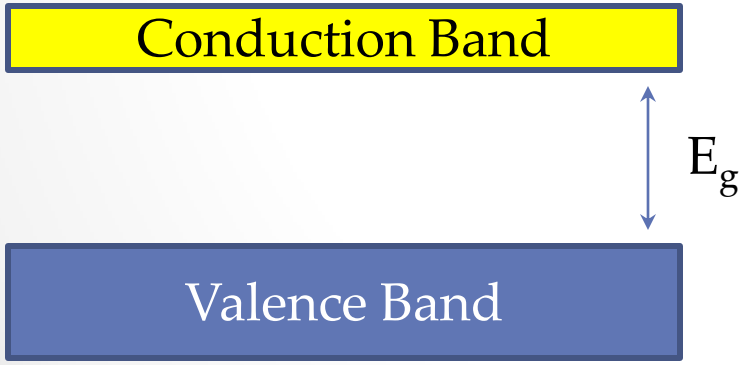


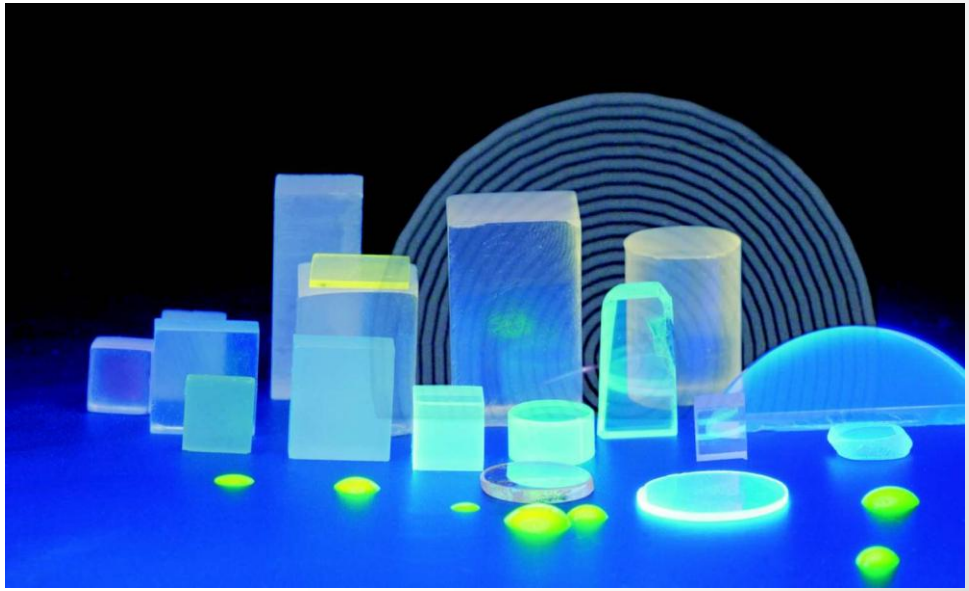


M. Suzuki and S. Kubota, *Mechanism of proportional scintillation in Argon, Krypton and Xenon*. Nuclear Instruments & Methods 164:197-199, 1976.

Inorganic Scintillators

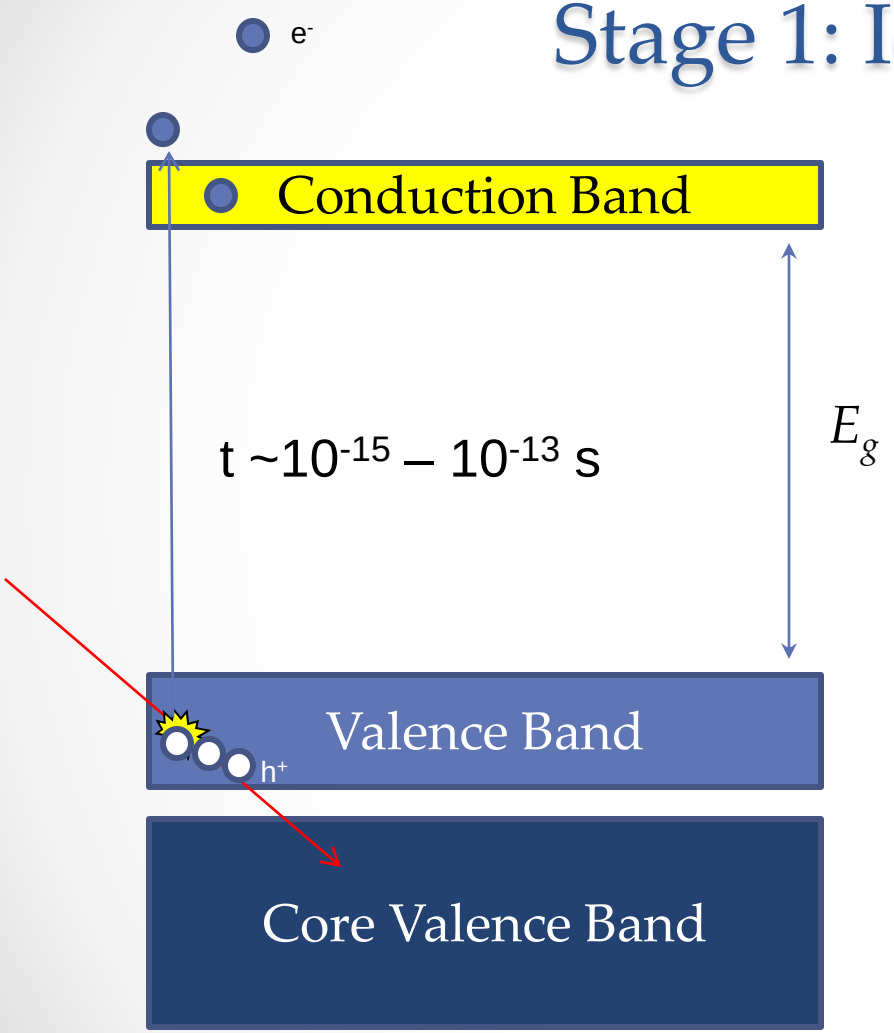
- Most inorganic scintillation mechanisms can be understood with semiconductor concepts
- Many physical mechanisms
- 3 "stages" of scintillation
  1. Ionization – creation of e^- - h^+ pair
  2. Charge carrier thermalization
  3. Luminescence





Inorganic Scintillators

Stage 1: Ionization



- Electron – hole pairs created
- Energy required ~2-7 times E_g

$$w_{e-h} = \beta E_g \qquad \beta \approx 3$$

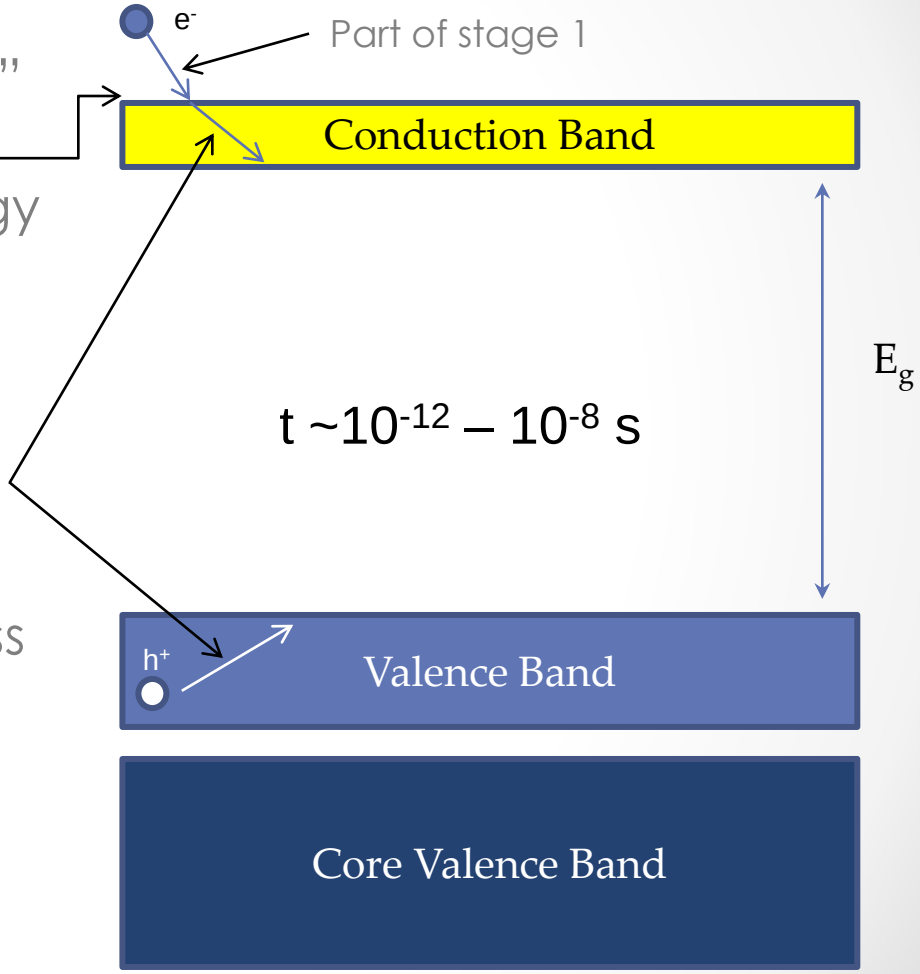
For most inorganic scintillators

- Followed by:
  - Secondary x-rays
  - Non-radiative decay (Auger processes – secondary electrons)
  - Inelastic electron – electron scattering
- Whole process lasts on the order of 10^{-15} – 10^{-13} s

Inorganic Scintillators

Stage 2: Thermalization

- "Preparation for luminescence"
- Process begins when the electron has lost enough energy to be below the ionization threshold
- More energy is lost through intraband transitions and electron-phonon relaxation
- Luminescent centers are excited – the excitation process depends on the physical properties of the scintillator
- Total time ~ 10^{-12} – 10^{-8} s
- Determines rise time of scintillator



Inorganic Scintillators

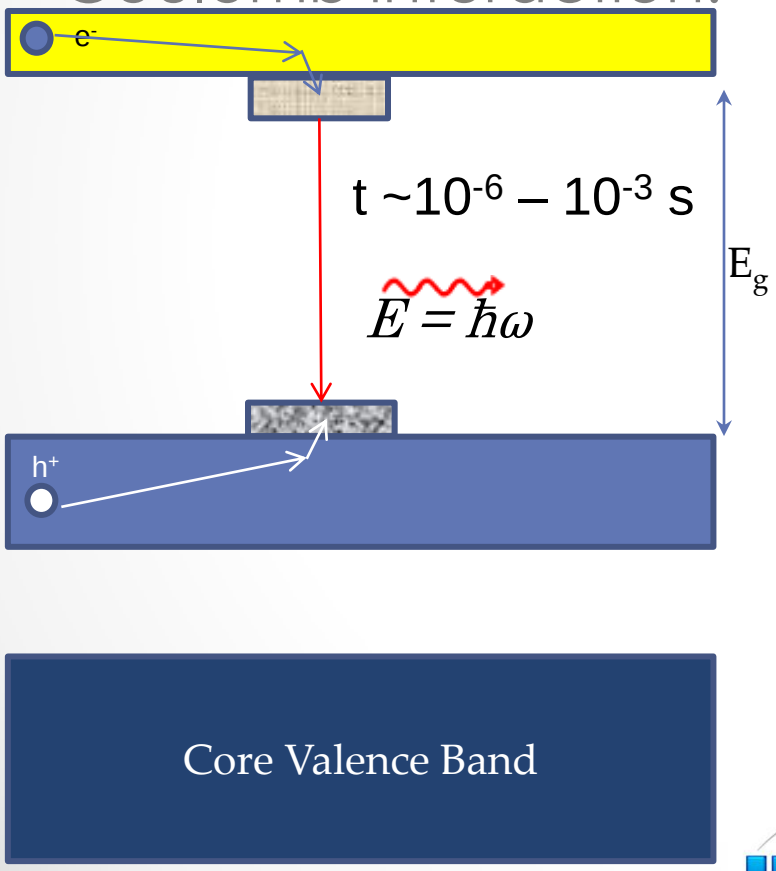
Stage 3: Luminescence

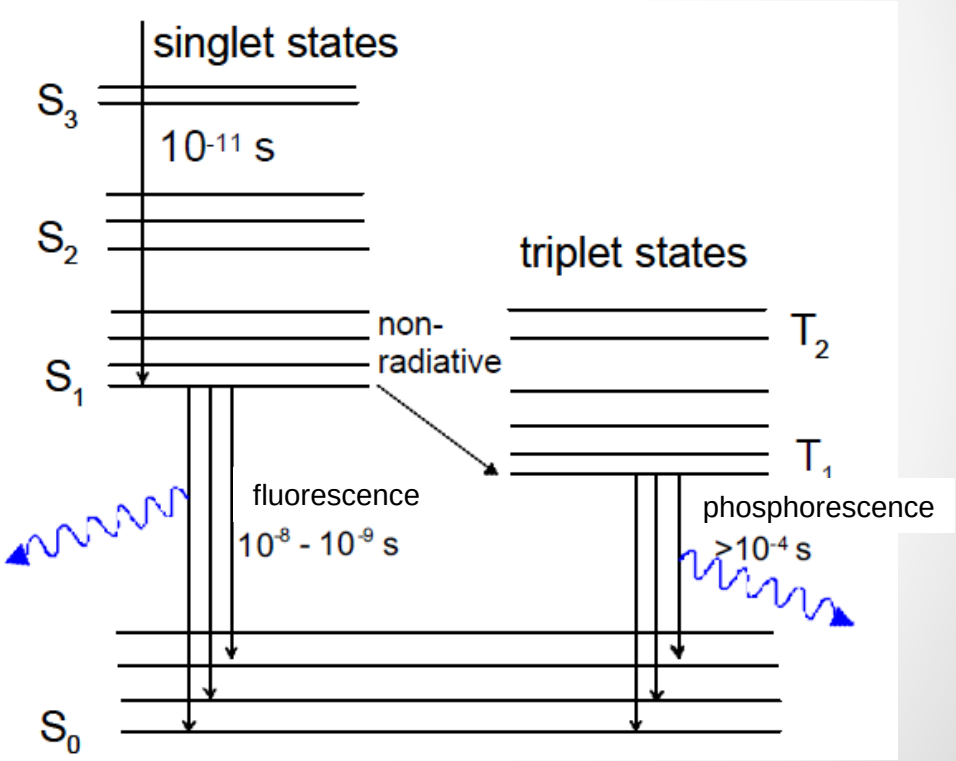
- Self-trapped exciton
- Core-valence
- Self-activated
- Dopant activated

Inorganic Scintillators

Self-trapped Exciton (STE) Luminescence I

- Exciton: Electron-hole pair attracted through the Coulomb interaction.





Inorganic Scintillators

Self-trapped Exciton Luminescence II

- Exciton: Electron-hole pair attracted through the Coulomb interaction.
- Free excitons are highly mobile and delocalized in 'perfect' crystals.
- Excitons interact with small perturbations of an imperfect lattice (dislocations, interstitials, etc.) and become trapped.
- In most cases it creates singlet and triplet states with the triplet state dominating.
- The STE recombines radiatively with long decay time ~10^{-6} – 10^{-3} s (due to forbidden triplet state).

Inorganic Scintillators

Self-trapped Exciton Luminescence III

- Neutron sensitive example: $LiBaF_3$

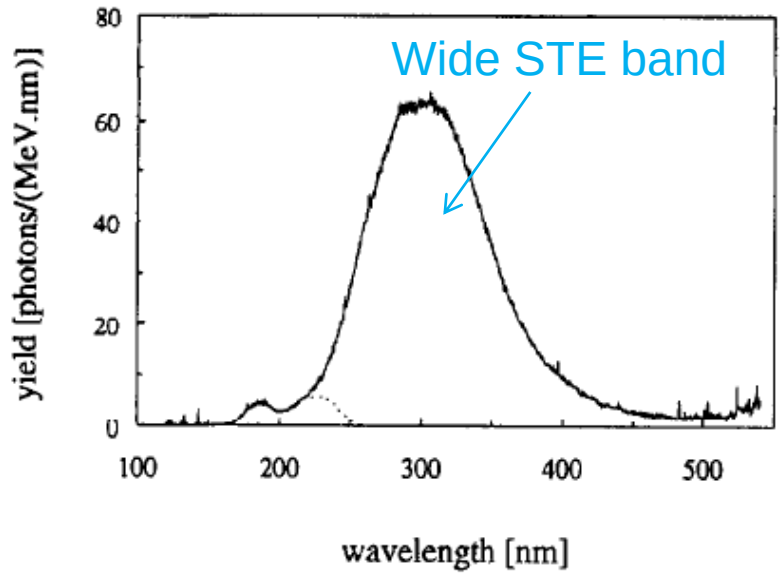


Fig. 1. The X-ray induced emission spectrum of $LiBaF_3$. The dashed line depicts the second emission band due to cross luminescence. At room temperature it is hidden under the broad self-trapped-exciton emission band.

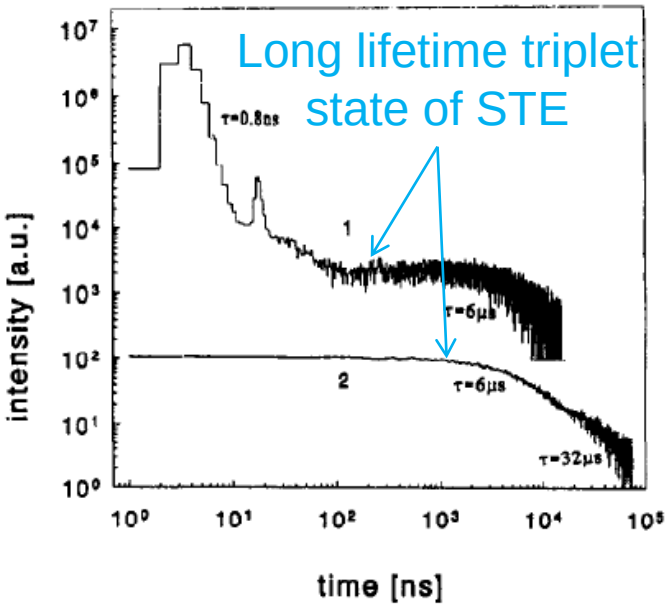
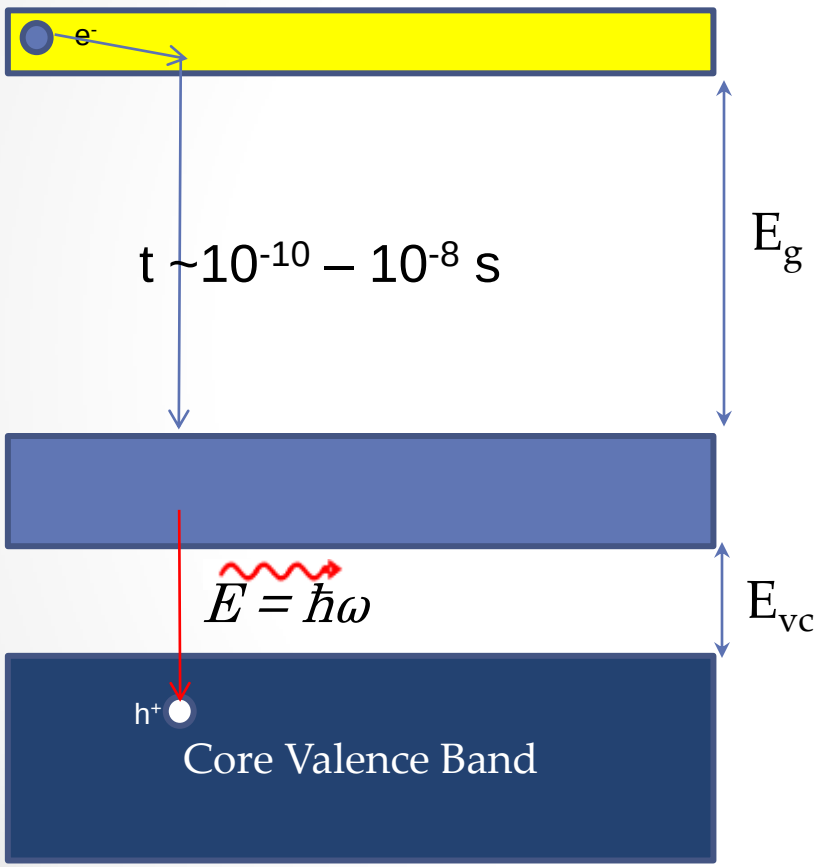


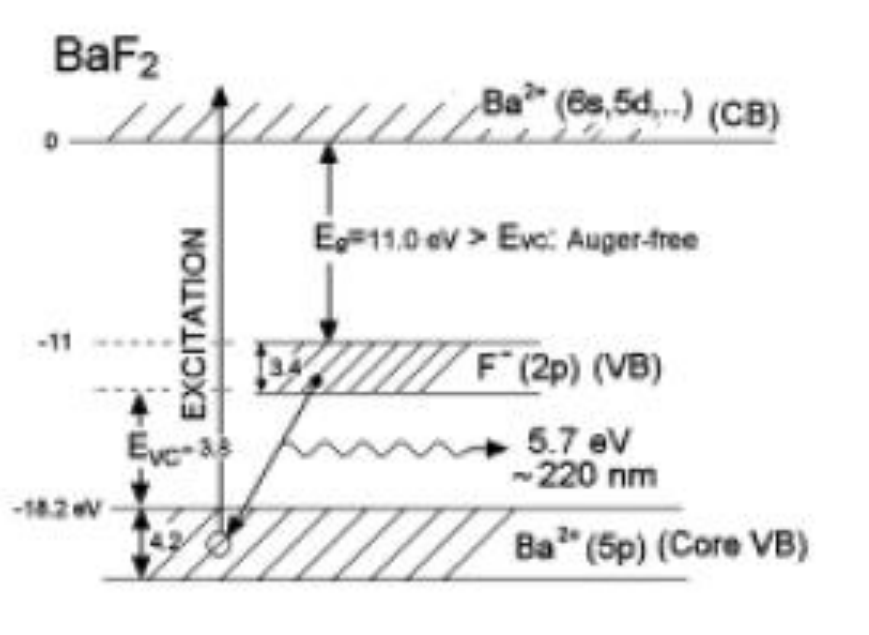
Fig. 2. Curve 1: decay curve of $LiBaF_3$ excited with ^{60}Co gamma rays, obtained with the single photon counting technique. The resolution is 1 ns/channel. Curve 2: decay curve of $LiBaF_3$ excited with ^{244}Cm alpha-particle ($E_\alpha \approx 4.25$ MeV at arrival in the crystal). The spectrum is an average over 1000 events recorded with a LeCroy LS140 digital oscilloscope.

M. J. Knitel, et al. *LiBaF3, a thermal neutron scintillator with optimal neutron-gamma discrimination.* Nuclear Instruments & Methods in Physics Research Section A, 374:197-201, 1996.

Inorganic Scintillators

Core-Valence Luminescence I





CVL – $LiBaF_2$ example

Inorganic Scintillators

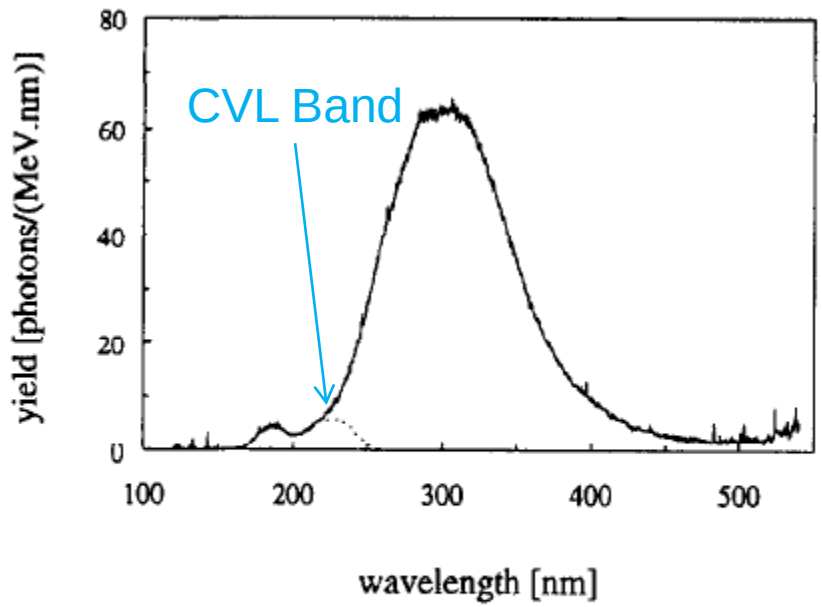
Core-Valence Luminescence II

- Ionization occurs from the core valance band
- An electron from the outer valence band recombines radiatively with a hole from the core valence band
- E_{vc} needs to be less than E_g to avoid Auger process
- There is a very slow non-radiative decay from the conduction band to the valence band
- CVL is typically very fast ~10^{-9} s
- UV emission

Inorganic Scintillators

Core-Valence Luminescence III

- Neutron sensitive example: LiBaF3



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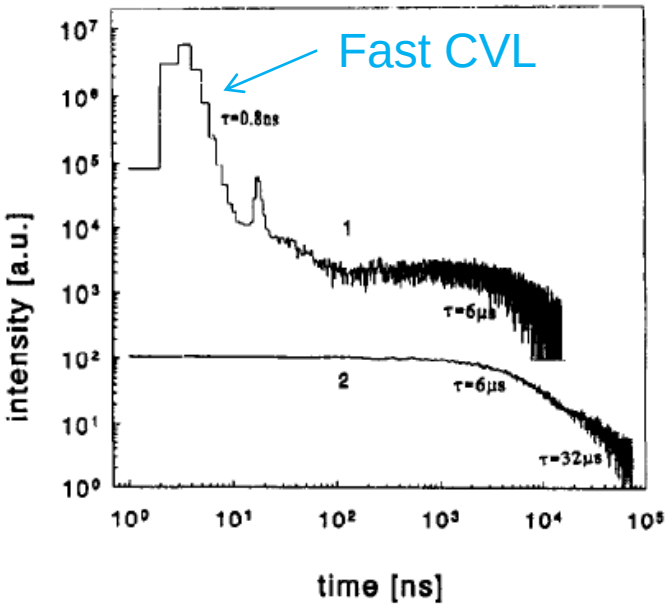

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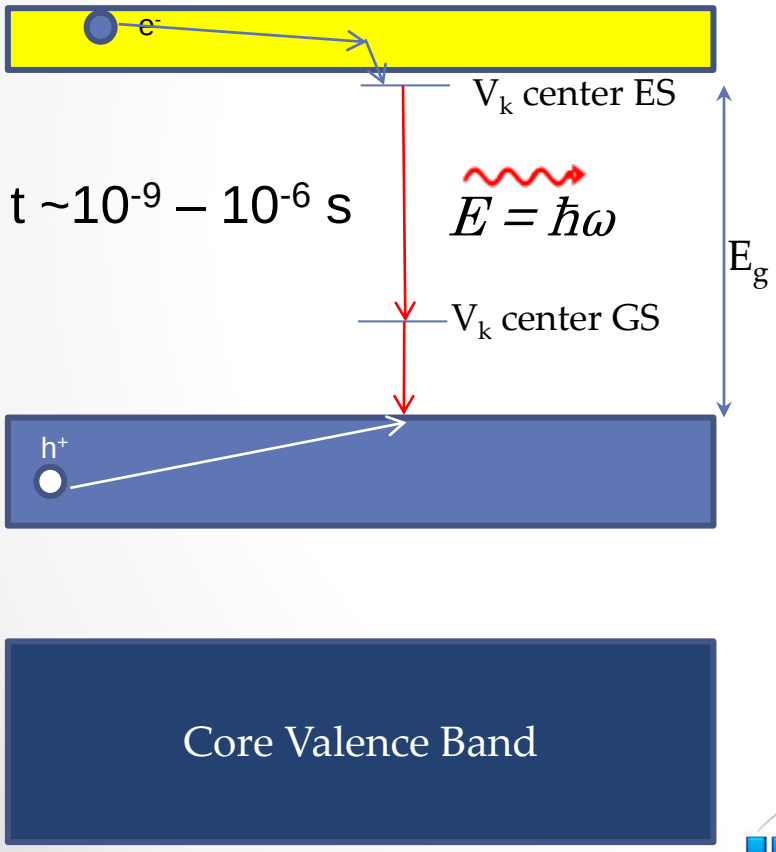
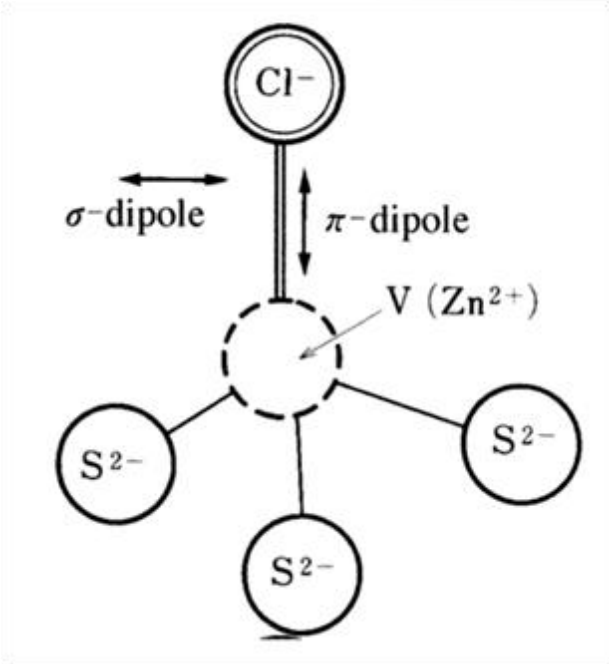
Inorganic Scintillators

Self-activated Luminescence I

Stoichiometric excess (interstitial) or deficiency (vacancy)





ZnS SA structure

Note: Cl^- ion is called a co-activator and is needed for charge compensation but is still termed self-activated

Inorganic Scintillators

Self-activated Luminescence II

- Self-activation results from either an excess or deficiency of host lattice ions
- Excess ions result in interstitials while deficiencies result in vacancies (V_k centers)
- Electron is trapped by the luminescent center putting the center in its excited state
- The center relaxes radiatively
- Decay is ~ 10^{-9}-10^{-7} s determined by the center's decay time.

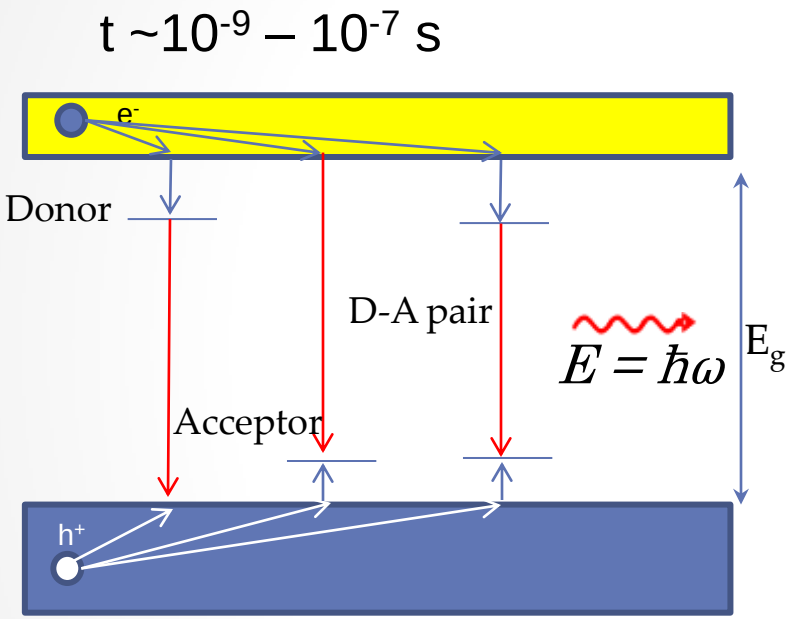
Inorganic Scintillators

Self-activated Luminescence III

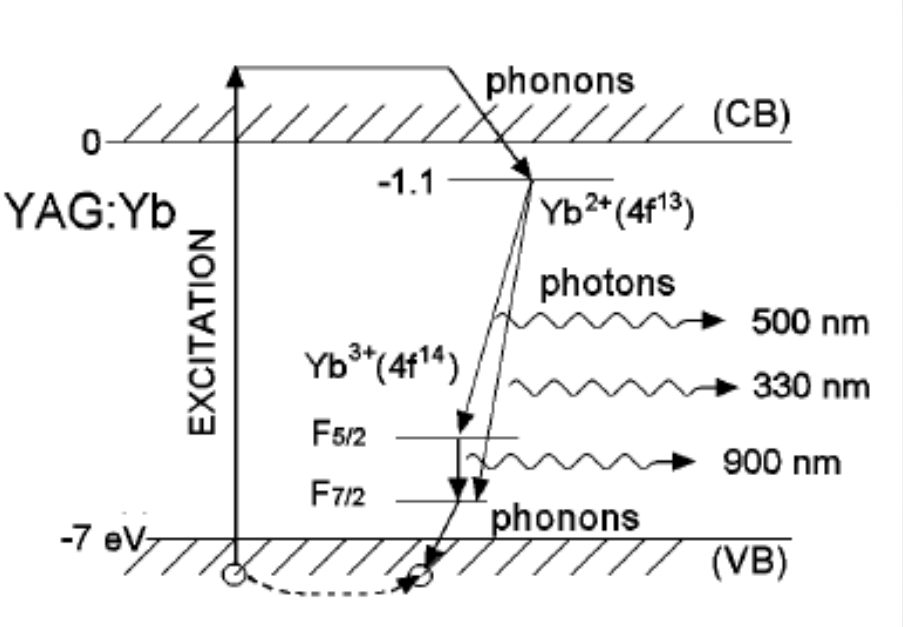
- Neutron Sensitive example: (LiF)ZnS:Cl, Cs_2LiYCl_6 and Li_3TaO_4
- Self-activated luminescence is generally inefficient leading to low light yields
- Doping the scintillator produces many more photons
- It is therefore uncommon to see neutron scintillators that rely on self-activation, i.e. ZnS:Ag,Cl and $Cs_2LiYCl_6:Ce^{3+}$ are much more common.

Inorganic Scintillators

Dopant Activated Luminescence I



Simple activator type luminescence



Charge transfer – YAG:Yb example

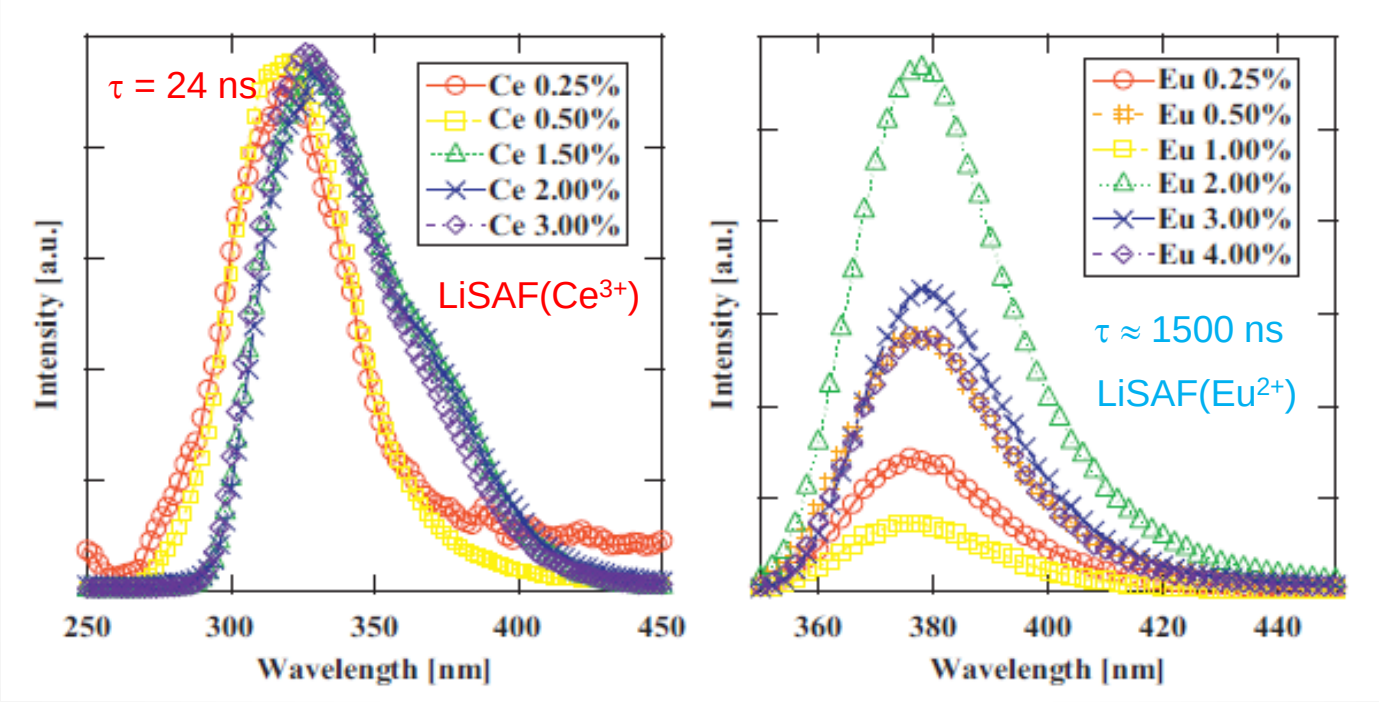
Inorganic Scintillators

Dopant Activated Luminescence II

- Activator ion is a substitute for a host lattice ion (i.e. Ag^{2+} replaces Zn^{2+} in ZnS:Ag)
- This creates allowed states in the band gap
- An electron is trapped on the activator site putting it in an excited state and relaxes radiatively
- Decay is ~ 10^{-9}-10^{-6} s determined by the activator's decay time.
- Most dominant mechanism is simple recombination on the activator, but in some materials charge transfer occurs from the ligand to the cation
  - This forms a charge transfer band which bypasses forbidden transitions.

Inorganic Scintillators
Dopant Activated Luminescence III

- Neutron sensitive examples: Many standard scintillators = $^{6}LiF/ZnS:Ag$, $LiGlass:Ce^{3+}$, $LiSrAlF_6:Eu^{2+}$
  Charge transfer = $Li_2Lu_5O_4(BO_3)_3:Yb$

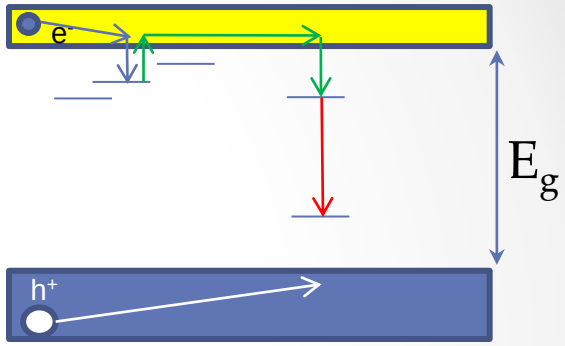


Yamaji, A. et al. *Crystal growthandscintillationpropertiesofCeandEudopedLiSrAlF6*. Nucl. Instr. Meth. A, **659** (2011), 368-372

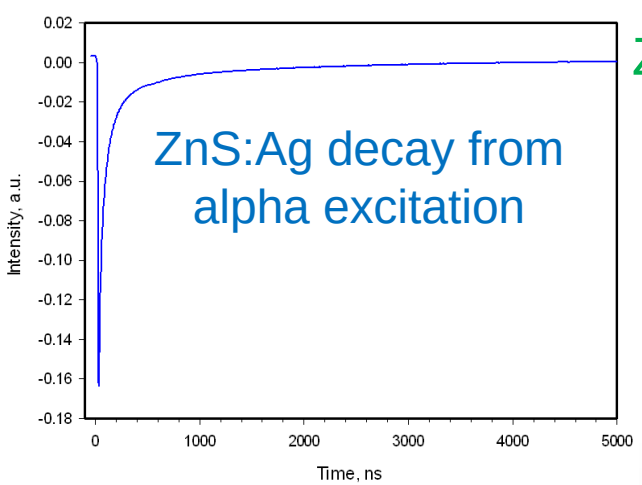
Aside: Factors Influencing Decay Time

- Fluorescence and phosphorescence
- Speed of energy transfer
- Number of luminescence centers
  - More centers = faster decay
- Impurities (electron or hole traps)
  - Shallow traps will temporarily hold charges
  - Some scintillators are also storage phosphors

} Cause of afterglow



BE CAREFUL WHEN LOOKING AT QUOTED DECAY TIMES!



ZnS decay time is rarely quoted the same:

~100 ns

~1000 ns

~10000 ns

Why? Afterglow confuses the situation!

Scintillators for Thermal Neutron Detection Questions and (some) Answers

- What is the best scintillator to use?
  - That depends…
- Because there is a large (n,p) scattering cross-section with Hydrogen and it is a low Z material, would it be best to use organic scintillators (i.e. Plastics) – they are fast?
  - Hint: consider the energy of the incident neutron
- But what about Borated or Lithiated plastics/liquids?
- What neutron converter is best for inorganic scintillators?
- Don't forget what characteristics are important
  - Light yield, emission spectrum, decay time, etc.
- Many scintillators have multiple luminescence mechanisms!
  - Can you use that to your advantage?

^{10}B vs ^{6}Li vs ^{odd}Gd in Scintillators

- $n + {}^{3}He \rightarrow {}^{3}H + {}^{1}H + 0.764$ MeV
- $n + {}^{6}Li \rightarrow {}^{4}He + {}^{3}H + 4.79$ MeV
- $n + {}^{10}B \rightarrow {}^{7}Li^{*} + {}^{4}He \rightarrow {}^{7}Li + {}^{4}He + 0.48$ MeV γ +2.3 MeV (93%)
  $\rightarrow {}^{7}Li + {}^{4}He$ +2.8 MeV (7%)
- $n + {}^{155}Gd \rightarrow Gd^{*} \rightarrow \gamma$-ray spectrum $\rightarrow$ conversion electron spectrum
- $n + {}^{157}Gd \rightarrow Gd^{*} \rightarrow \gamma$-ray spectrum $\rightarrow$ conversion electron spectrum
- Things to consider:
  - Energy/range of reaction products
  - Light yield
  - Hygroscopicity

^{10}B containing Neutron Scintillators

- ^{10}B usually used in plastic or liquid scintillators
- ZnS:Ag ($^{10}B_2O_3$) – Newly developed
- LiB_3O_5 and $Li_2B_4O_7$
- High density Boron Nitride
  - Ceramic

^{6}Li containing Inorganic Neutron Scintillators

Host	Dopant (conc mol%)	Density ρ (g/cm^3)	ρZ^4_{eff} ($\times 10^{-6}$)[a]	Abs. Length at 1.8Å (mm)	Light yield photons per		α/β Ratio	λ_{em} (nm)	τ (ns)
					Neutron	MeV gamma			
^{6}Li-glass	Ce	2.5		0.52	~6000	~4000	0.3	395	75
^{6}LiI	Eu	4.1	31	0.54	50,000	12,000	0.87	470	1400
^{6}LiF/ZnS	Ag	2.6	1.2	0.8	160,000	75,000	0.44	450	>1000
$LiBaF_3$	Ce,K	5.3	35		3500	5000	0.14	190–330	1/34/2100
$LiBaF_3$	Ce,Rb	5.3	35		3600	4500	0.17	190–330	1/34/2400
$^6Li_6^{dep}Gd(^{11}BO_3)_3$	Ce	3.5	25	0.35	40,000	25,000	0.32	385,415	200/800
$^6Li_6^{dep}Gd(^{11}BO_3)_3$	Ce	} 3.9		} 1	40,000	30,000		420	200/800
$+Y_2SiO_5$	Ce				—	30,000		420	70
$Cs_2^6LiYCl_6$	Ce (0.1)	3.3		3.2	70,000	22,000	0.66	380	~1000
					—	700		255–470	3
$Cs_2^6LiYBr_6$	Ce (1)	4.1		3.7	88,000	23,000	0.76	389,423	89/2500

[a] As an indication of gamma-ray detection efficiency by photoelectric effect ρZ^4_{eff} values are presented

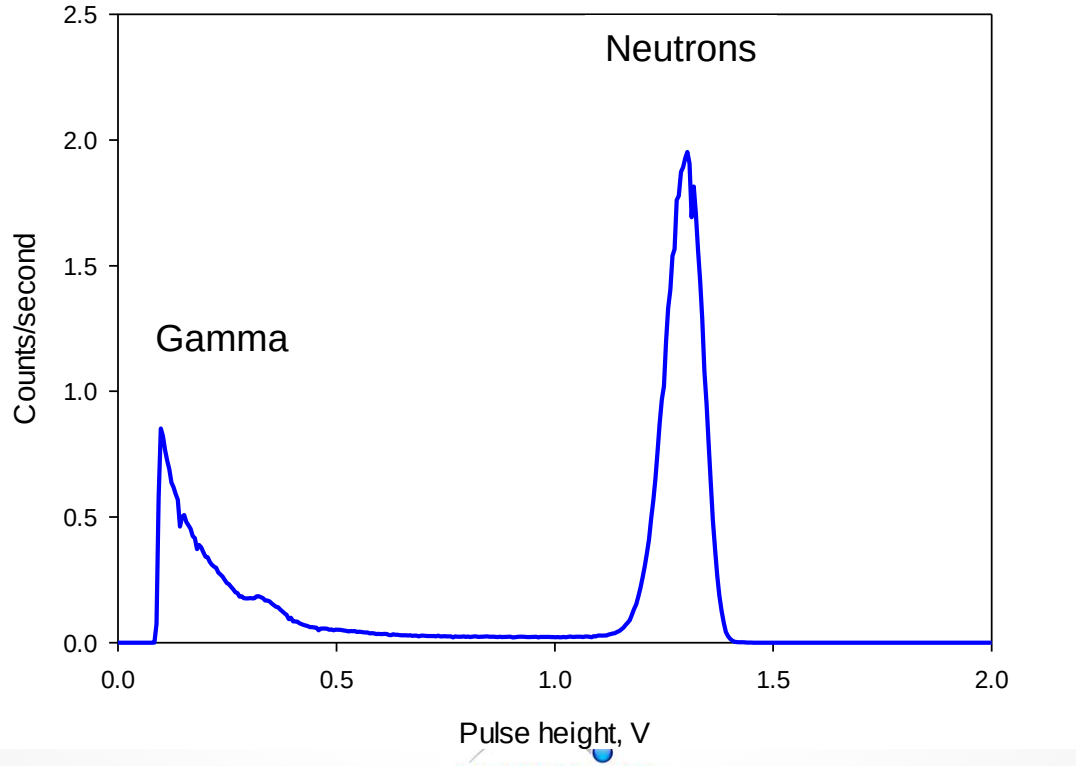
C.W.E. van Eijk, A. Bessière, P. Dorenbos, *Inorganic thermal-neutron scintillators*, Nucl. Instr. Meth. A **29** (2004) 260-267

Already used in neutron scattering facilities

Using Scintillation Properties to Your Advantage

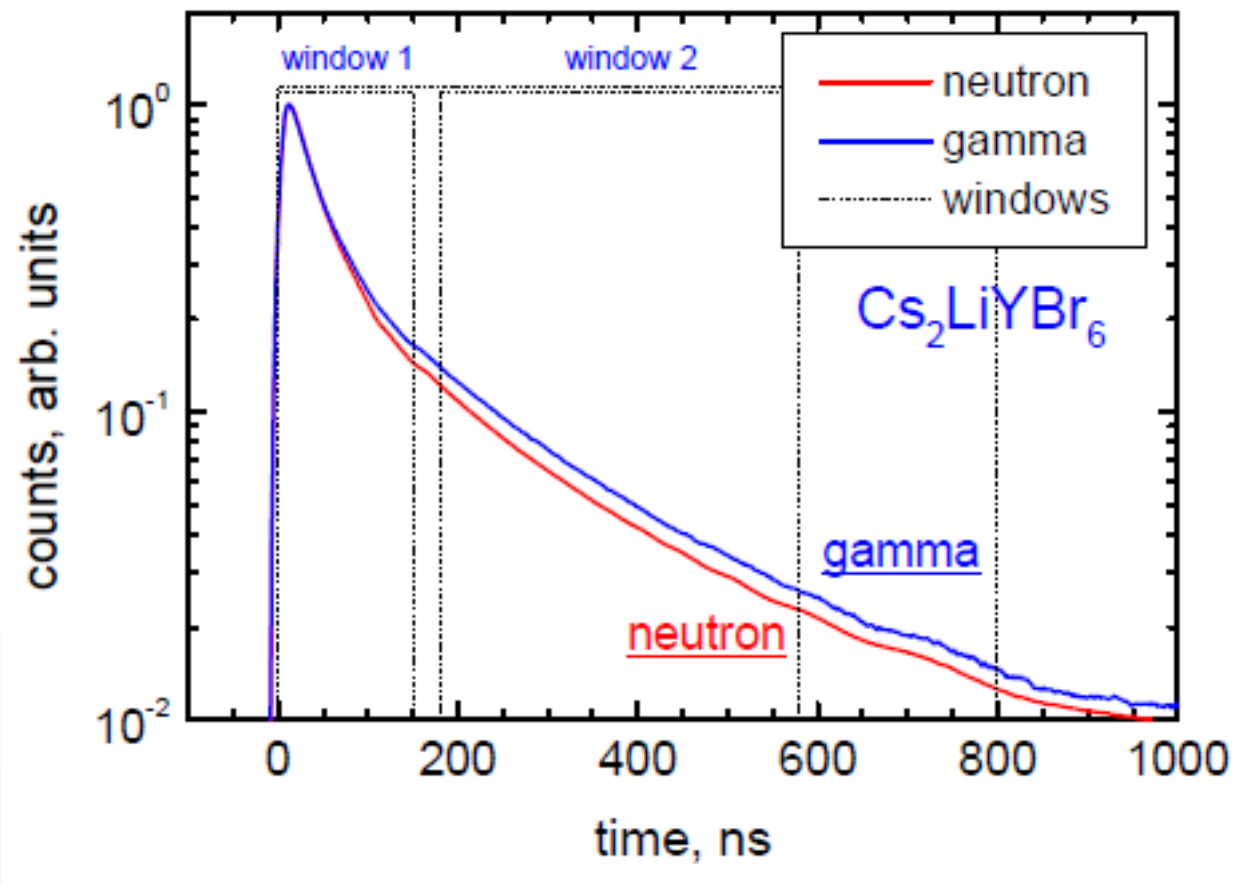
- Pulse height discrimination – example ^{6}Li-Glass:Ce

Host	Dopant (conc mol%)	Density ρ (g/cm^3)	ρZ^4_{eff} ($\times 10^{-6}$)^a	Abs. Length at 1.8Å (mm)	Light yield photons per		α/β Ratio	λ_{em} (nm)	τ (ns)
					Neutron	MeV gamma			
^{6}Li-glass	Ce	2.5		0.52	~6000	~4000	0.3	395	75



Using Scintillation Properties to Your Advantage

- Pulse shape discrimination



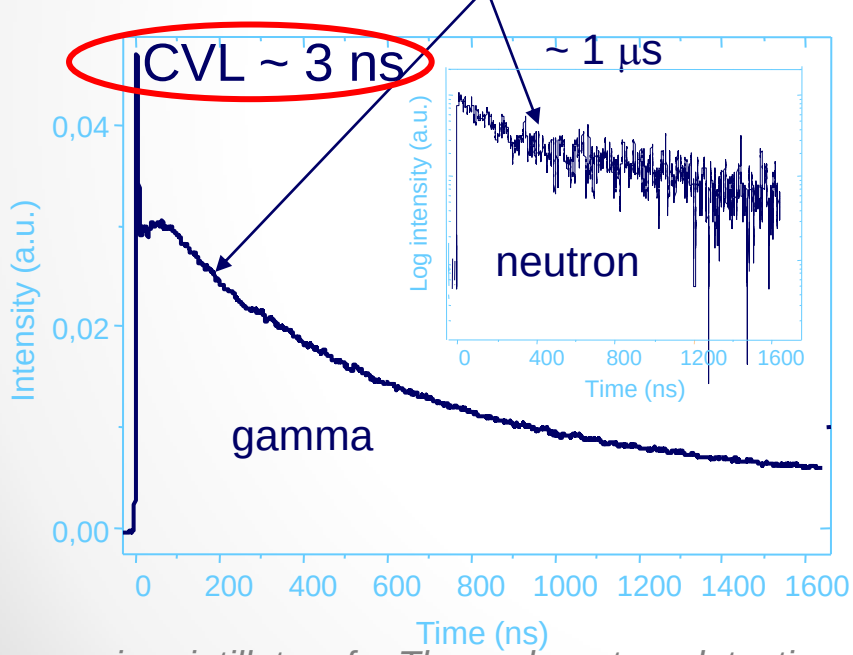
Using Scintillation Properties to Your Advantage

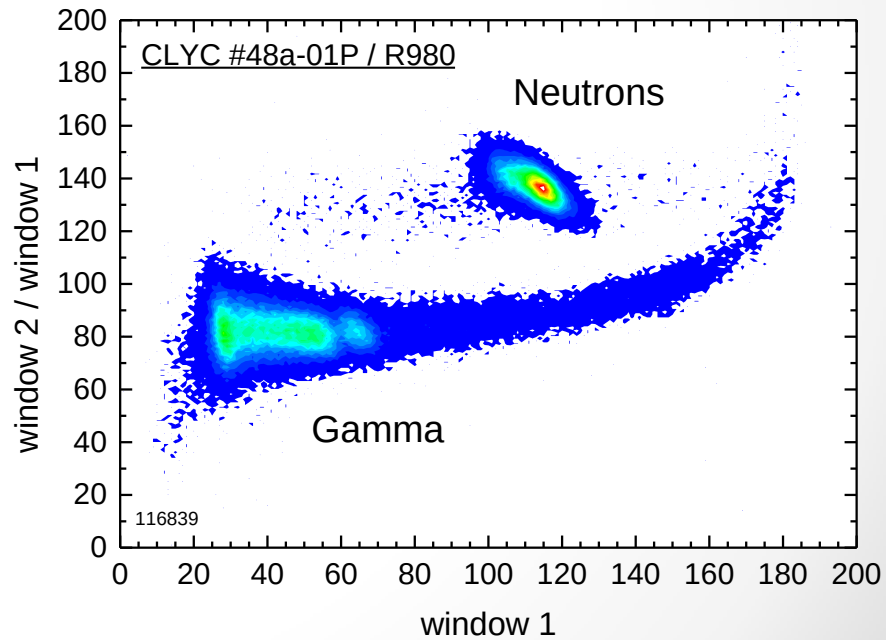
- Pulse shape discrimination - example: $Cs_2LiYCl_6:Ce^{3+}$

Host	Dopant (conc mol%)	Density ρ (g/cm^3)	ρZ^4_{eff} ($\times 10^{-5}$)[a]	Abs. Length at 1.8Å (mm)	Light yield photons per Neutron	Light yield photons per MeV gamma	α/β Ratio	λ_{em} (nm)	τ (ns)
$Cs_2^6LiYCl_6$	Ce (0.1)	3.3		3.2	70,000	22,000	0.66	380	~1000
					—	700		255-470	3

Slow response

Caution: Hygroscopic and limited availability



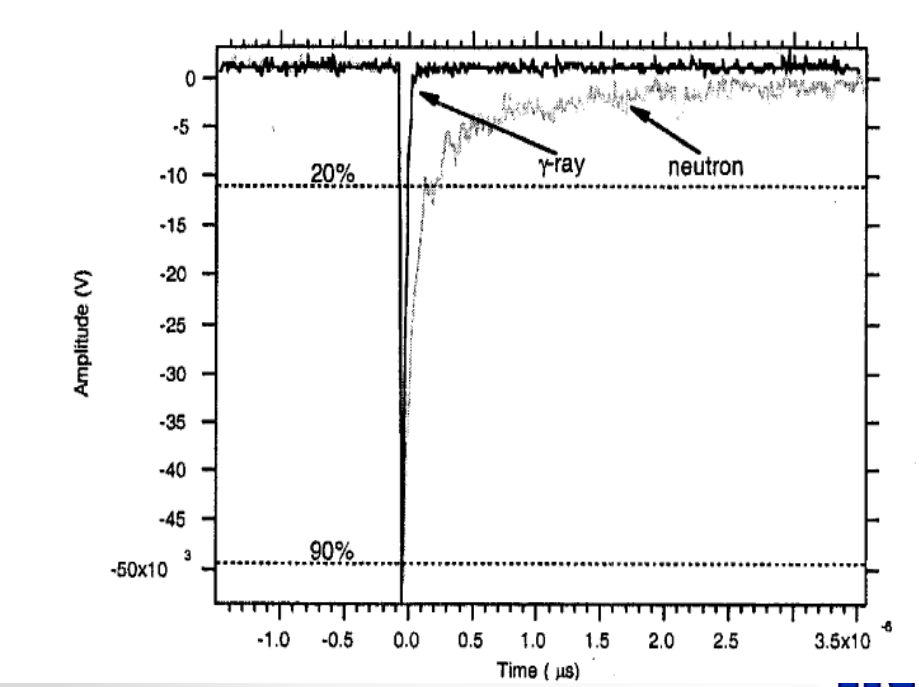


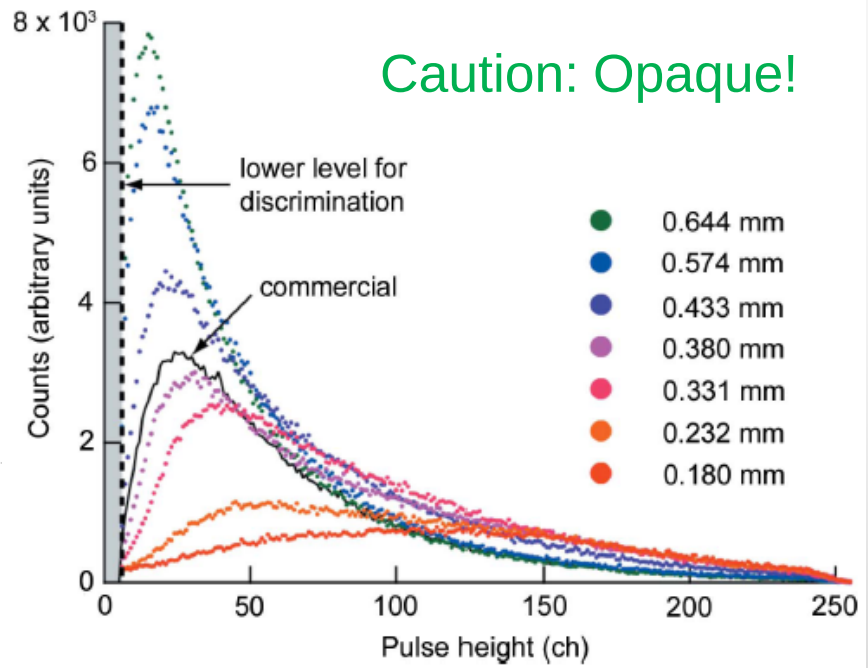
Inorganic scintillators for Thermal-neutron detection.
C.W.E. van Eijk Presentation at IEEE (2004)

Using Scintillation Properties to Your Advantage

- Pulse height and pulse shape discrimination – example (^{6}LiF)ZnS:Ag

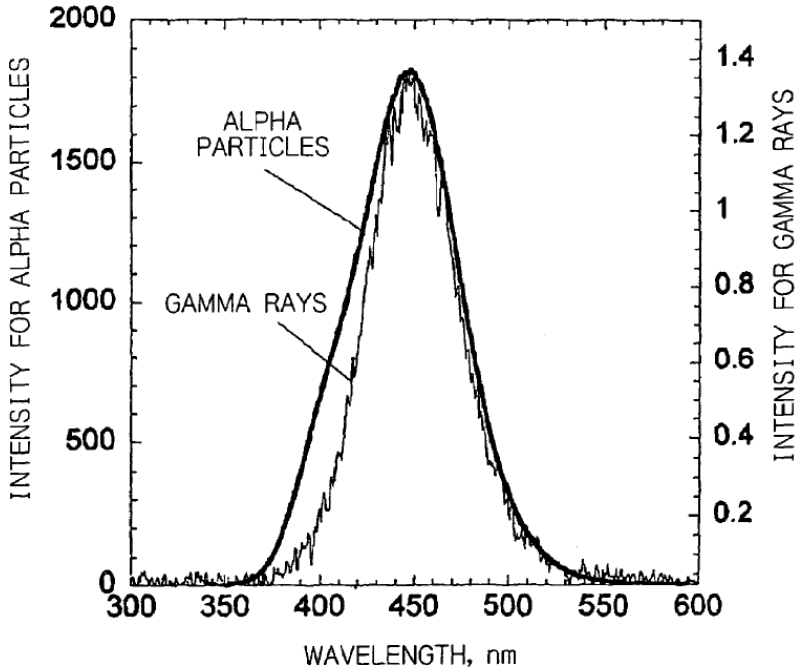
	em.wavel (nm)	γ-ray LY (ph/MeV)	decay (ns)	FWHM (%) at 662 keV	neutron LY (ph/n)	decay (ns)	FWHM (%)	α/β
^{6}LiF/ZnS Ag	450	75,000	~100	-	160,000	>10000	-	0.44





Using Scintillation Properties to Your Advantage

- Pulse height and emission spectra discrimination – example (^{6}LiF)ZnS:Ag:Cl



Particle detector and neutron detector that use ZnS phosphors.
Katagiri, M., US patent #US 7679064 (2004)

Using Scintillation Properties to Your Advantage

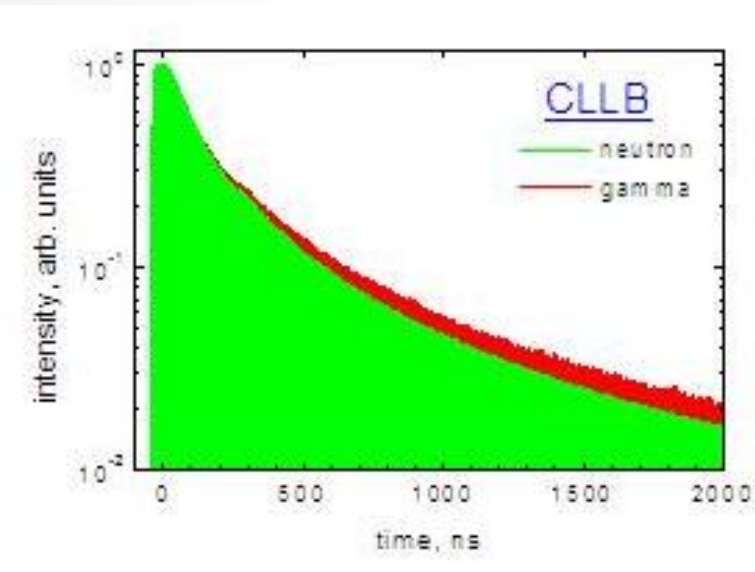
$Cs_2LiLaBr_6:Ce^{3+}$ **(CLLB)**

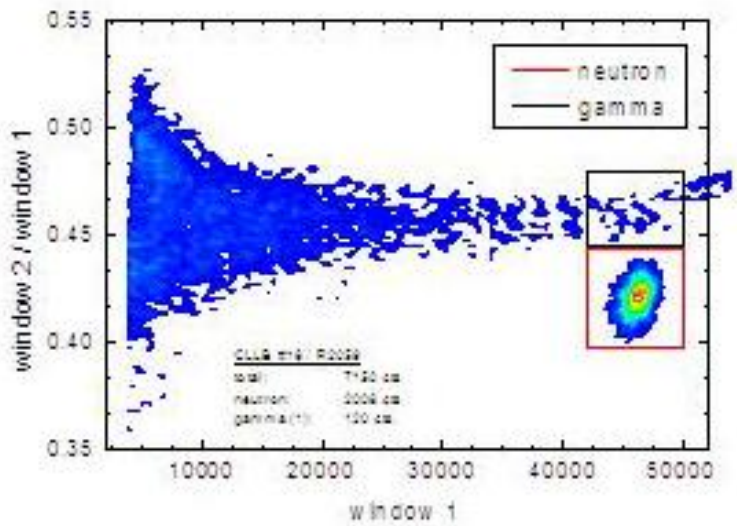
	dopant	em.wavel (nm)	γ-ray LY (ph/MeV)	decay (ns)	FWHM (%) at 662 keV	neutron LY (ph/n)	decay (ns)	FWHM (%)	α/β
$Cs_2LiLaBr_6$	Ce	410	60,000	55,>270	2.9	180,000	55,>270		0.62

Caution: Hygroscopic and must be thick

Achieve ≤10^{-6} gamma sensitivity?

≥ LiF/ZnS:Ag





Inorganic scintillators for Thermal-neutron detection.
C.W.E. van Eijk Presentation at IEEE (2004)

Conclusions and More

- Scintillators are very powerful tools for neutron detectors.
- Choosing the appropriate scintillator requires consideration of a multi-parameter space weighted towards the application; in other words:
  - There are many different scintillators with different properties.
  - Choose the scintillator based on the application.
    - Be careful though!
  - Utilise the scintillator properties by collecting the light appropriately.
  - And by processing the signals appropriately.

Conclusions and More

Final word of caution: Be sure to check the neutron activation cross-sections for all materials in the scintillator!!!

LiI:Eu

Element	Isotope	Abundance (Percent)	Product Half-Life	$\sigma_{n,\gamma}$ (barns)
Europium	^{151}Eu	47.82	96 min $^{152}Eu^{m_2}$	3.8 ± 1.9
			9 hour $^{152}Eu^{m_1}$	2800 ± 300
			12 year $^{152}Eu^{g}$	5300 ± 300
	^{153}Eu	52.18	16 years	400 ± 100

Suggested Reading

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