Who needs better nuclear detector materials and how do we find them?

Stephen E. Derenzo
Department of Nuclear Medicine and Functional imaging
Life Sciences Division
Lawrence Berkeley National Laboratory






Stephen Derenzo | **Edith Bourret-Courchesne** | **Mattias Klintenberg** | **Bill Moses** | **Yetta Porter-Chapman** | **Marvin Weber**

Outline

- Limitations of Available Detector Materials
- Why are Crystals So Important?
- First-Principles Calculations and Grand Challenges
- General Selection Rules for Detector Materials
- Finding Materials for Specific Classes of Detectors
  - Semiconductor charge collection detectors (e.g. CZT)
  - Cerium-activated scintillators (e.g. $LaBr_3$:Ce)
  - Semiconductor scintillators (e.g. ZnO:Ga)
- Conclusions

Who Needs Better Detector Materials?

- Nuclear Medicine needs an efficient scintillator with <200 ps timing resolution for time-of-flight positron emission tomography (PET)
- Homeland Security needs an ambient temperature, efficient, fast, rugged, low-cost gamma-ray detector with sufficient energy resolution (<2% fwhm at 662 keV) to detect and identify radioisotopes

Limitations of Available Semiconductor Detector Materials

	Si	Ge†	CZT*	HgI2	PbI2	AlSb
Density (g/cc)	2.33	5.35	5.76	6.36	6.16	4.22
Atten. Length** (mm)	44.6	23.7	20.1	13.9	14.1	27.2
Photofraction**	0.0016	0.043	0.18	0.38	0.40	0.16
Band gap (eV)	1.12(I)	0.67(I)	1.7	2.1(D)	2.4(D)	1.6(I)
E(pair) (eV)	3.6	3.0	5.0	4.2	4.9	5.1
$\mu(e^-)$	1400	40,000	1350	100	8	≈400
$\mu(h^+)$	480	40,000	120	4	2	≈500
Fano factor	≈0.1	0.08	>0.2			??
E(fwhm) 662 keV		0.2%	≈1%			??

†Ge must be cooled (LN) *$Cd_{0.9}Zn_{0.1}Te$ **511 keV

Limitations of Available Scintillators

(Primarily for gamma ray detection)

Desired properties	BGO	NaI(Tl)	BaF_2	LSO	Ideal
$\sigma_{photo}/(\sigma_{photo}+\sigma_{Compton})$ (.5 MeV)	0.43	0.18	0.19	0.34	$\geq$0.43
Density	7.1	3.7	4.9	7.4	>7
Photons per MeV	8,200	40,000	1800	≈20,000	>100,000
Energy resolution	13%	7%	10%	11%	<2%
Decay time (ns)	300	230	< 1	40	< 1
Photoelectrons/MeV/ns*	2.6	18	200	50	>10,000
Cost per CC	$10	low	low	$100	low

* Photoelectrons per ns = 0.1 (Photons) / (Decay time)

BGO = $Bi_4Ge_3O_{12}$ LSO = Lu_2SiO_5:Ce

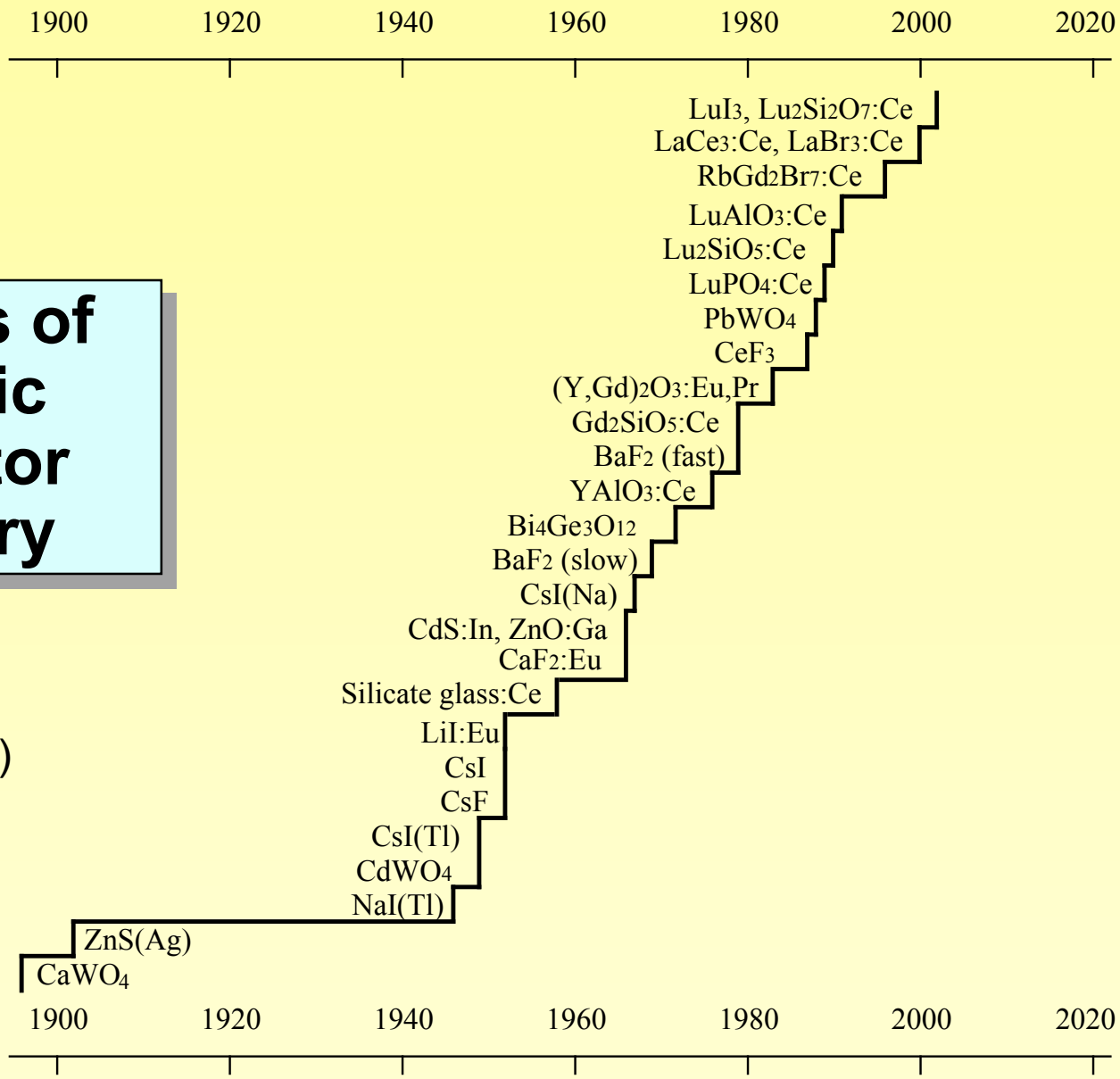
BGO Compared to Recently Discovered Cerium-Activated Scintillators

	BGO	LSO	LPS	LuYAP	LaBr3	LuI3
Luminosity (ph/MeV)	8,200	25,000	26,000	12,500	60,000	90,000
E(fwhm) (662 keV)	12%	10%	10%	8%	2.5%	<8%
Decay Time (ns)	300	40	38	25, 200	25	30
Density (g/cc)	7.1	7.4	6.2	7.4	5.3	5.6
Atten. Length* (mm)	11	12	15	13	22	18
Photofraction*	43%	34%	31%	27%	14%	29%
Wavelength (nm)	480	420	385	390	370	470
Natural Radioactivity?	No	Yes	Yes	Yes	No	Yes
Hygroscopic?	No	No	No	No	Yes	Yes

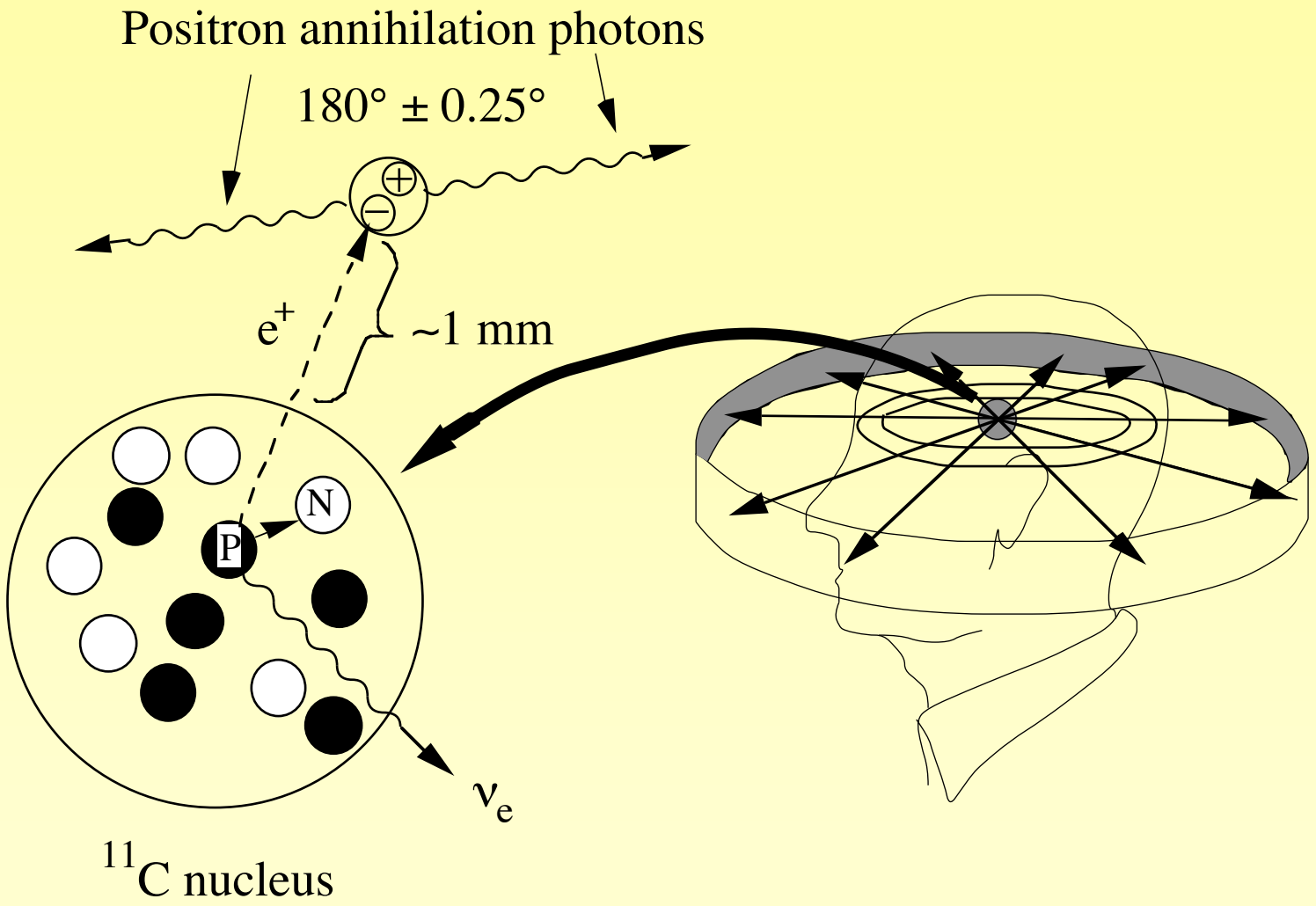
* 511 keV

105 Years of Inorganic Scintillator Discovery

(Marv Weber)



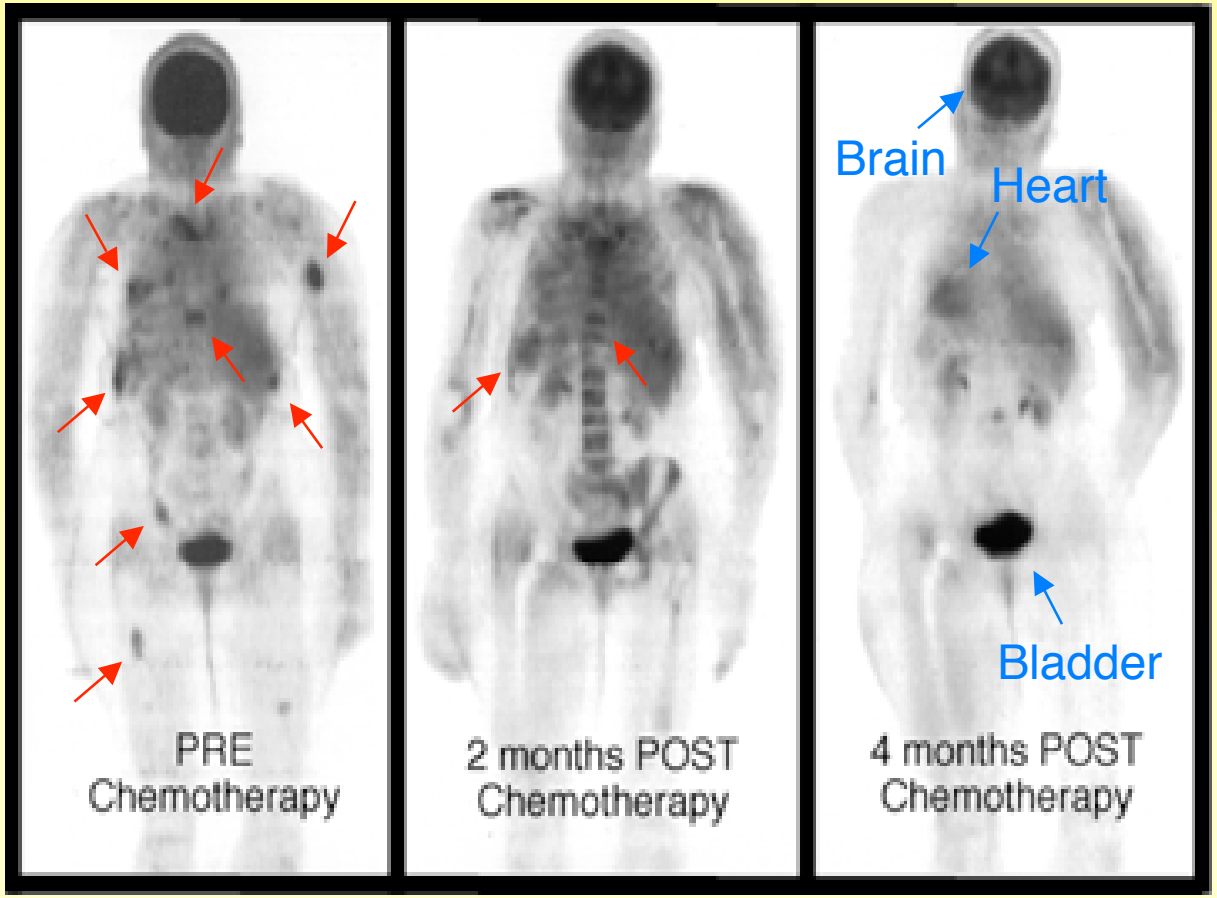
Positron Emission Tomography (PET)



Siemens ECAT 951 Positron Tomograph

PET Images of Breast Cancer Patient

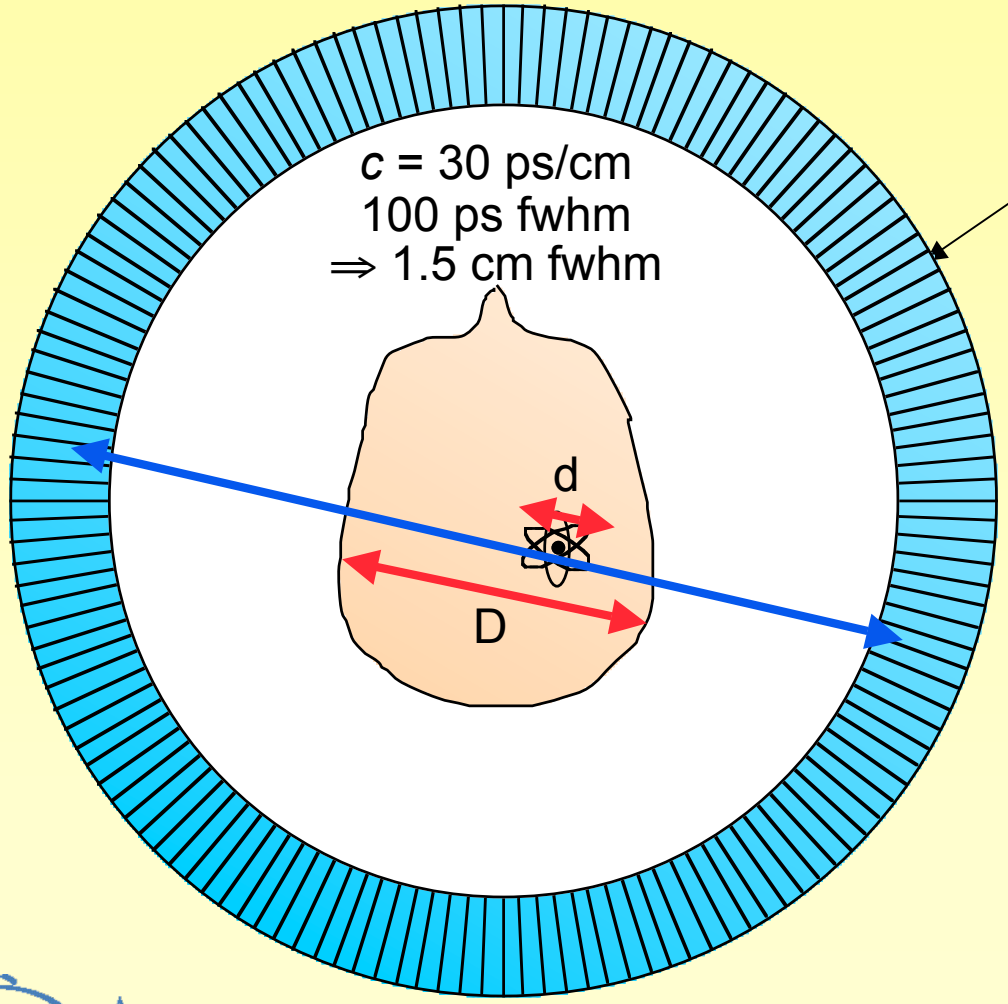
Metastases Shown with Red Arrows



Normal Uptake in Other Organs Shown in Blue

Tumors Easily Seen (~5 mm spatial resolution)

Time-of-Flight in PET Reduces Statistical Noise



Detectors

Time-of-Flight PET (at the 100 ps fwhm level) improves the noise-equivalent detection efficiency by a factor of 10 for the head and thorax, 15 for the abdomen

Outline

- Limitations of Available Detector Materials
- Why are Crystals So Important?
- First-Principles Calculations and Grand Challenges
- General Selection Rules for Detector Materials
- Finding Materials for Specific Classes of Detectors
  - Semiconductor charge collection detectors (e.g. CZT)
  - Cerium-activated scintillators (e.g. $LaBr_3$:Ce)
  - Semiconductor scintillators (e.g. ZnO:Ga)
- Conclusions

Why Are Crystals So Important?

- Semiconductor Charge Collection Detectors
  - High carrier mobility μ - requires long scattering times
  - Long carrier lifetime τ – requires no trapping on defects
  - Trapping length = μτE (want > 1 m)
- Scintillator Detectors
  - Want trapping on luminescent center >> trapping on defects
    Example:
    Ce-activated glass is a poor scintillator because carriers trap on defects before exciting the Ce.
    But if Ce are excited directly with UV, the fluorescence is efficient

What Crystals Can Exist?

"One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition"

John Maddox, editor of Nature, 1988

Three Computational Grand Challenges

1. Given a molecular formula, what stable periodic arrangements of atoms can exist at room temperature?
   (Number of combinations for 1-6 atoms >> 10^6)
2. Which of these are stable between room temperature and the melting point?
   (Important for growing crystals from the melt- less important for vapor deposition, hydrothermal growth, and transparent ceramics)
3. What is the optimal thermodynamic path for producing crystals with the minimum concentration of native defects?

Traditional Experimental Determination of Crystal Structure

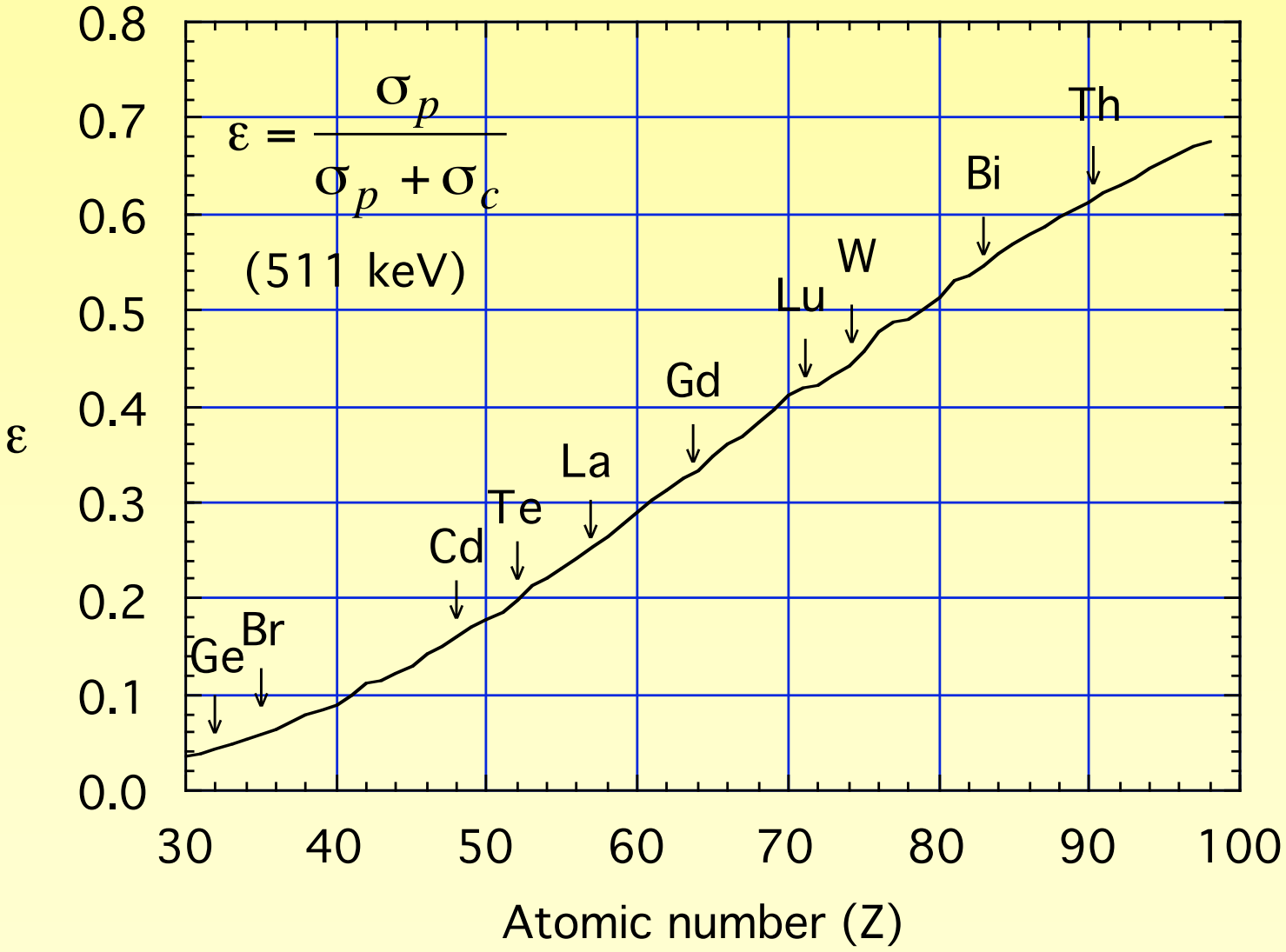
- Melting or thermal diffusion of integer ratios to attempt to make small crystals (e.g. GeO_2 and Bi_2O_3 in 3:2 ratio produces $Bi_4Ge_3O_{12}$)
- X-ray beam ==> Laue diffraction pattern
- Solve for the periodic atomic coordinates
- Publish synthesis and structure in Acta Crystallographica
- Discard crystals
- 96,000 entries in the 2005 Inorganic Crystal Structure database (ICSD)

Thousands of heavy crystals are known but have not been explored as nuclear detector materials

General Selection Rules for Detector Materials

- Good stopping power (density, atomic number)
- Low production cost
- Mechanical strength (want attractive atomic bonds)
- High yield of electrons and holes
- Band gap (<2.0 eV for semiconductor, >5 eV for cerium-activated scintillator)

511 keV Photofraction vs. Z



Outline

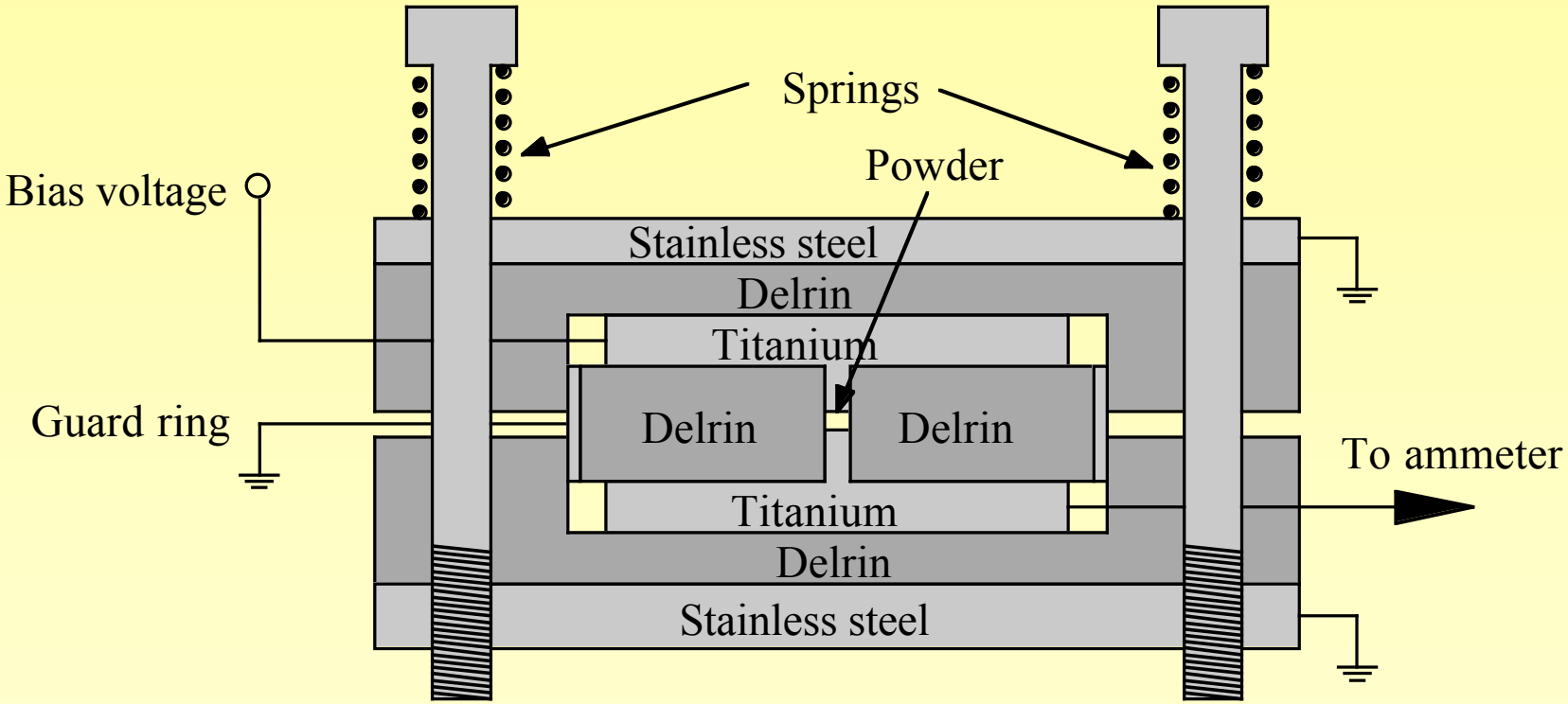
- Limitations of Available Detector Materials
- Why are Crystals So Important?
- First-Principles Calculations and Grand Challenges
- General Selection Rules for Detector Materials
- Finding Materials for Specific Classes of Detectors
  - Semiconductor charge collection detectors (e.g. CZT)
  - Cerium-activated scintillators (e.g. $LaBr_3$:Ce)
  - Semiconductor scintillators (e.g. ZnO:Ga)
- Conclusions

Semiconductor Charge Collection Detectors

General selection critera, plus:

- Carrier mobility [eff. mass/scattering time]
- Ultra-pure starting materials, esp. low concentration of carrier trapping impurities
- Crystal growth conditions that minimize the concentration of native defects that trap carriers [Grand Challenge #3]
- Low Fano factor [Variance/Poisson]

Pressure Cell for Semiconductor Discovery



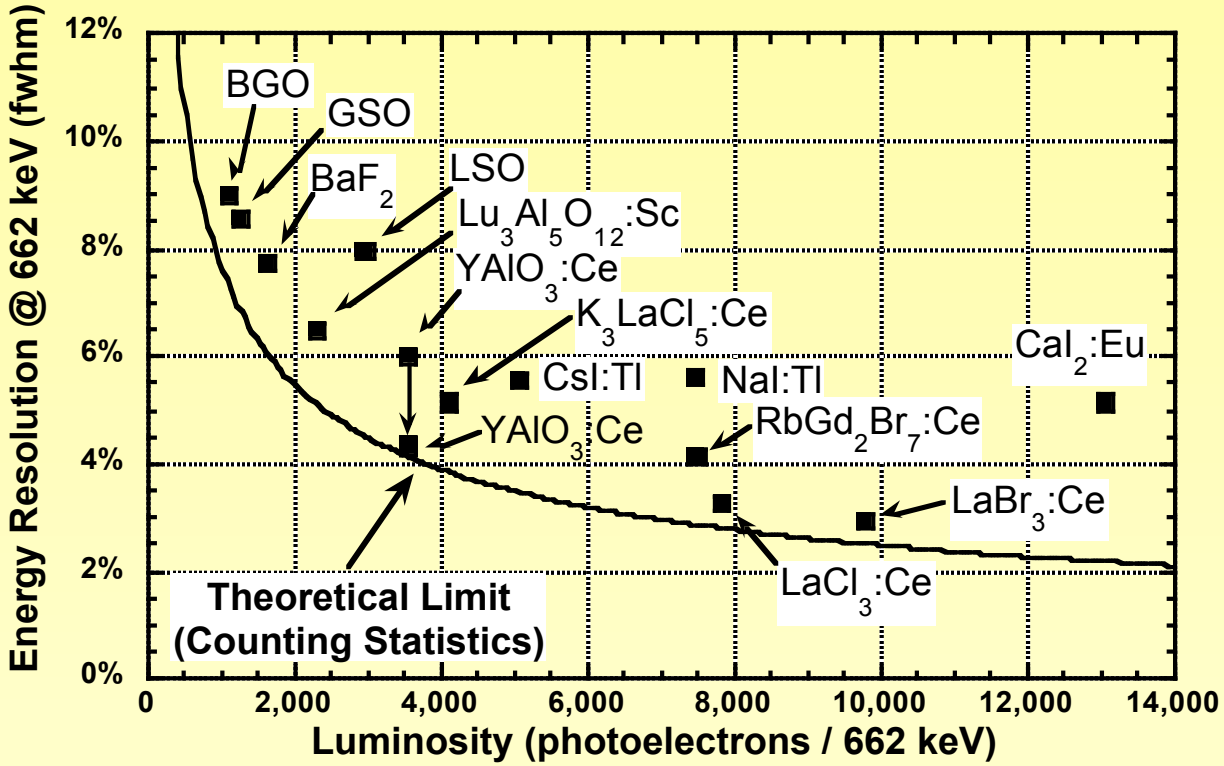
More at IEEE NSS Puerto Rico, Oct 23-29, 2005

Cerium-Activated Scintillators

General selection criteria plus:

- Band gap (>5 eV oxides & halides, >3 eV sulfides)
- Energy per electron-hole pair $\leq$10 eV
- Efficient hole trapping on Ce^{3+} [Ce 4f energy level]
- Efficient electron trapping on Ce^{4+} [Ce 5d energy level]
- Efficient radiative transition [No quenching]
- Fundamental limit 100,000 photons/MeV
- Linear scintillation response [$\Delta L/\Delta E$ constant]
- Fundamental limit 2% fwhm at 662 keV
- 20-40 ns decay time

Energy Resolution Depends on Linearity as Well as Light Output



Measured energy resolution of several scintillators for 662 keV gamma rays as a function of their light output (expressed as the number of photoelectrons observed with a photomultiplier tube). The solid curve indicates the theoretical lower limit placed by counting statistics. From P. Dorenbos, "Light output and energy resolution of Ce3+ doped scintillators," *Nucl Instr Meth,* vol. A486, pp. 208-213, 2002.

Light Output per keV can Depend on Electron Energy

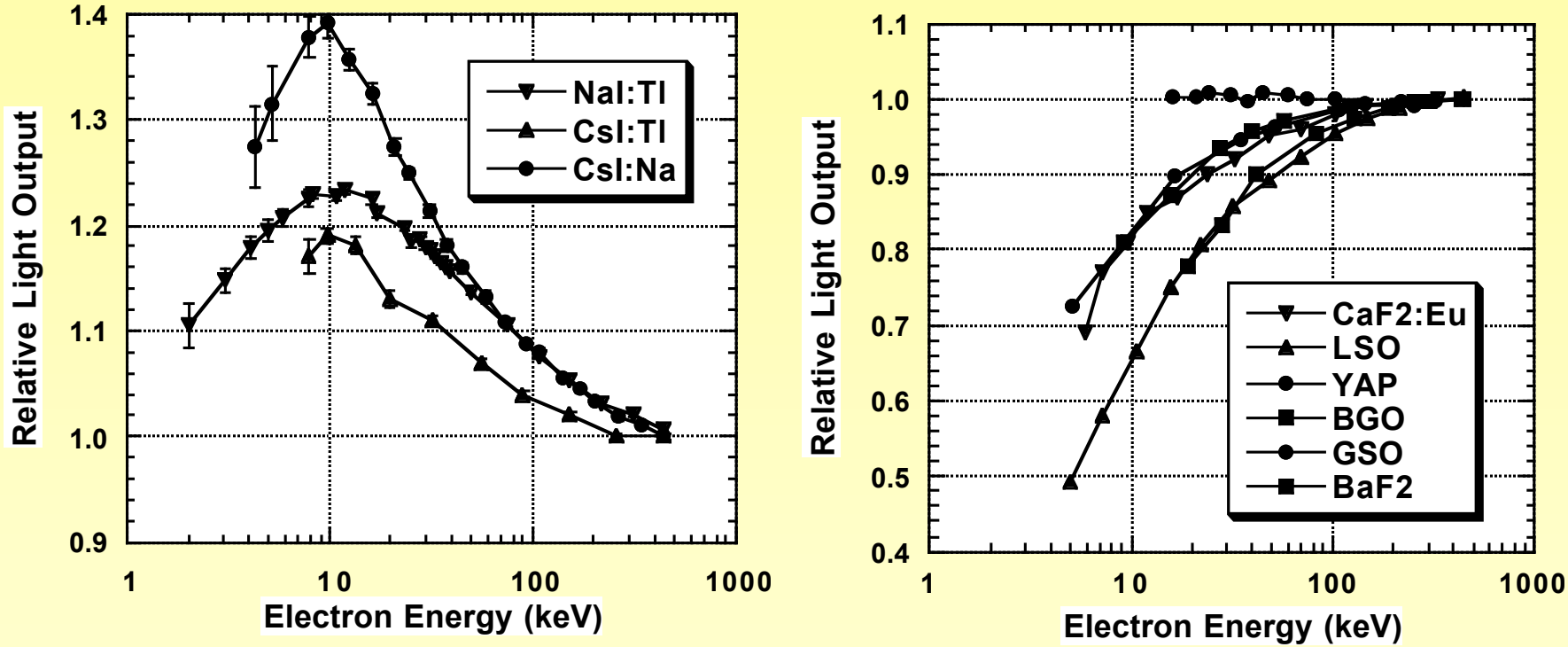
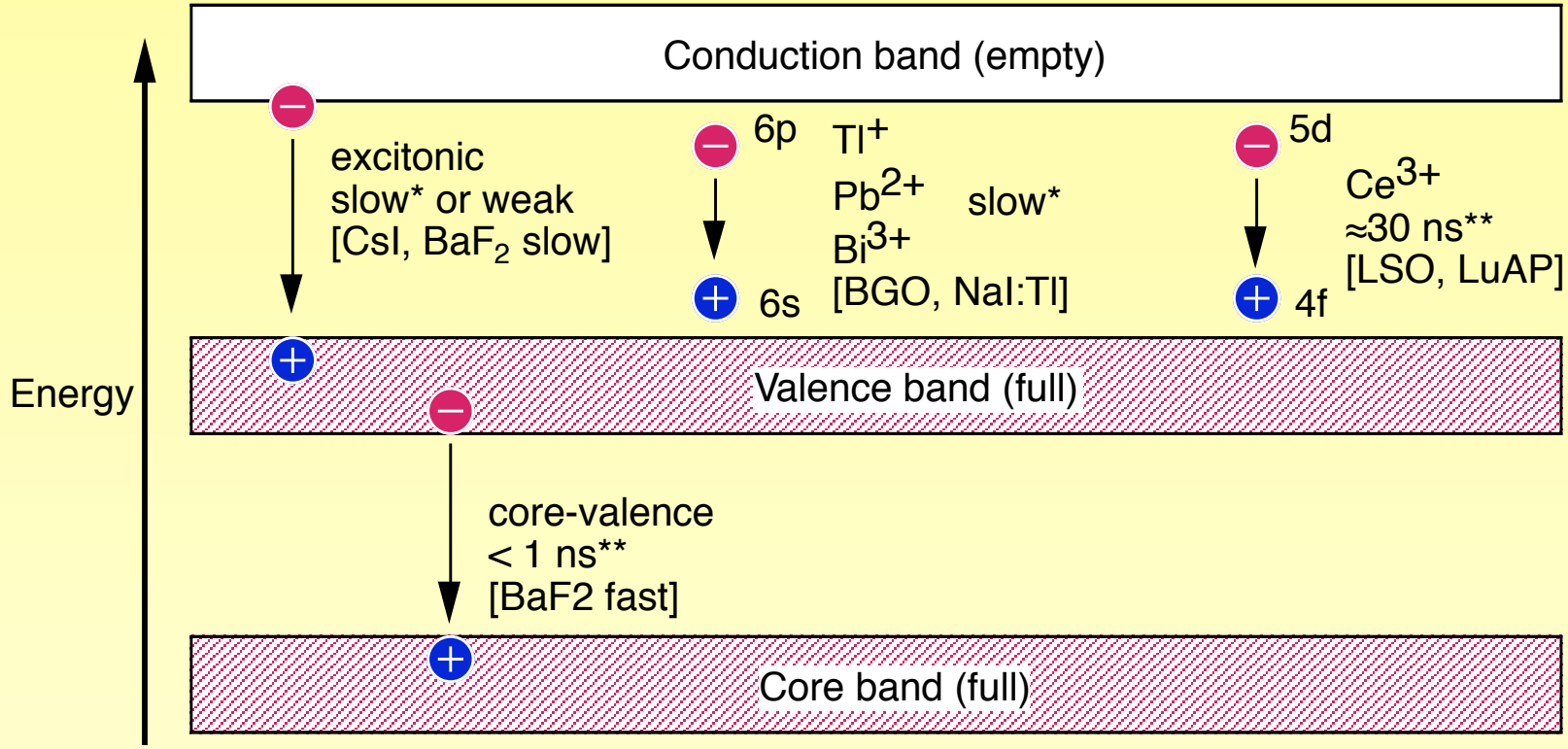


Figure 8.8 From W. Mengesha, T. Taulbee, B. Rooney and J. Valentine, "Light yield nonproportionality of CsI(Tl), CsI(Na), and YAP," *IEEE Trans Nucl Sci,* vol. 45, pp. 456-461, 1998.

Why is No Available Scintillator Both Bright and Fast (< 1 ns)?

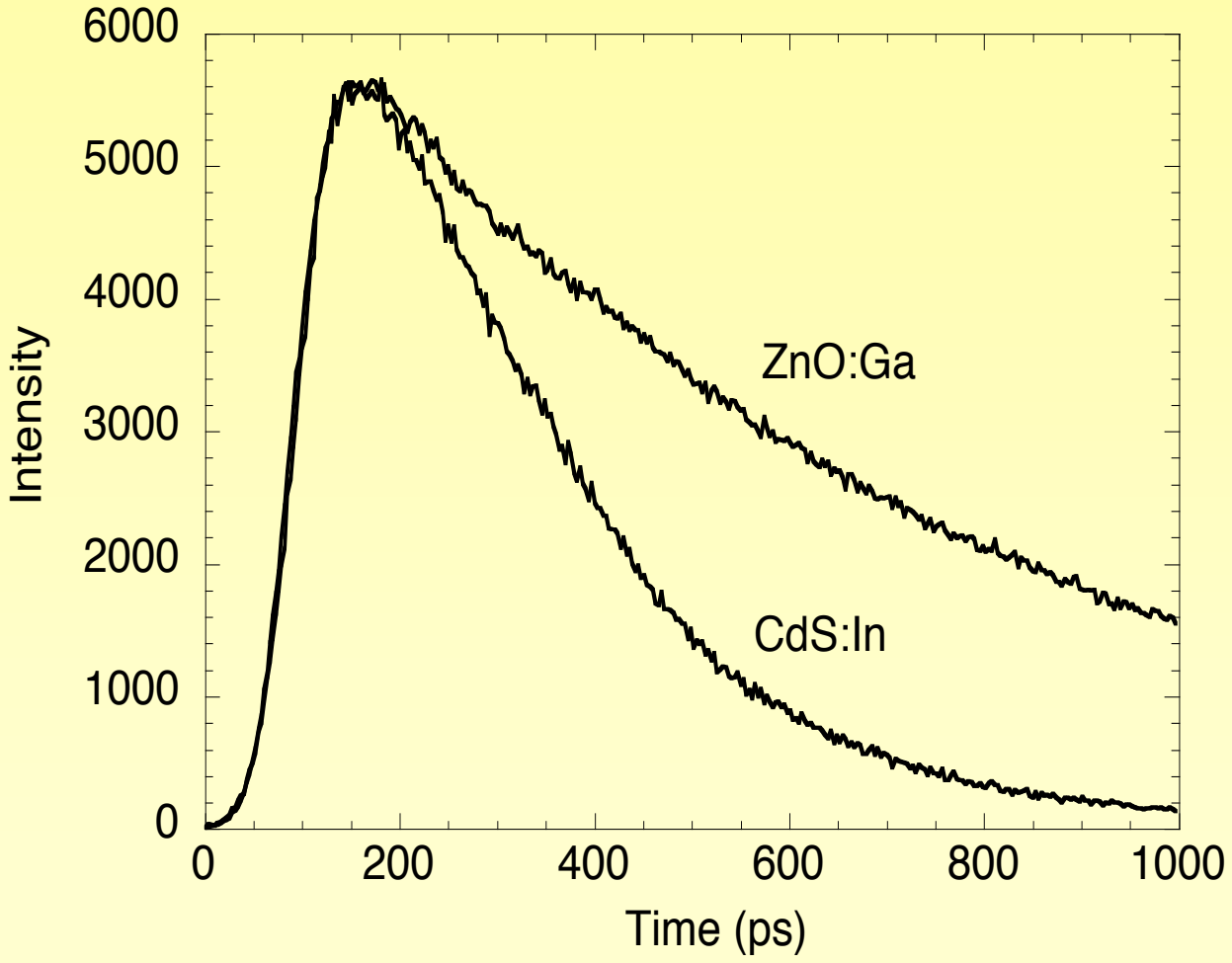


* triplet-> singlet forbidden
** allowed electric dipole

Outline

- Limitations of Available Detector Materials
- Why are Crystals So Important?
- First-Principles Calculations and Grand Challenges
- General Selection Rules for Detector Materials
- Finding Materials for Specific Classes of Detectors
  - Semiconductor charge collection detectors (e.g. CZT)
  - Cerium-activated scintillators (e.g. $LaBr_3$:Ce)
  - Semiconductor scintillators (e.g. ZnO:Ga)
- Conclusions

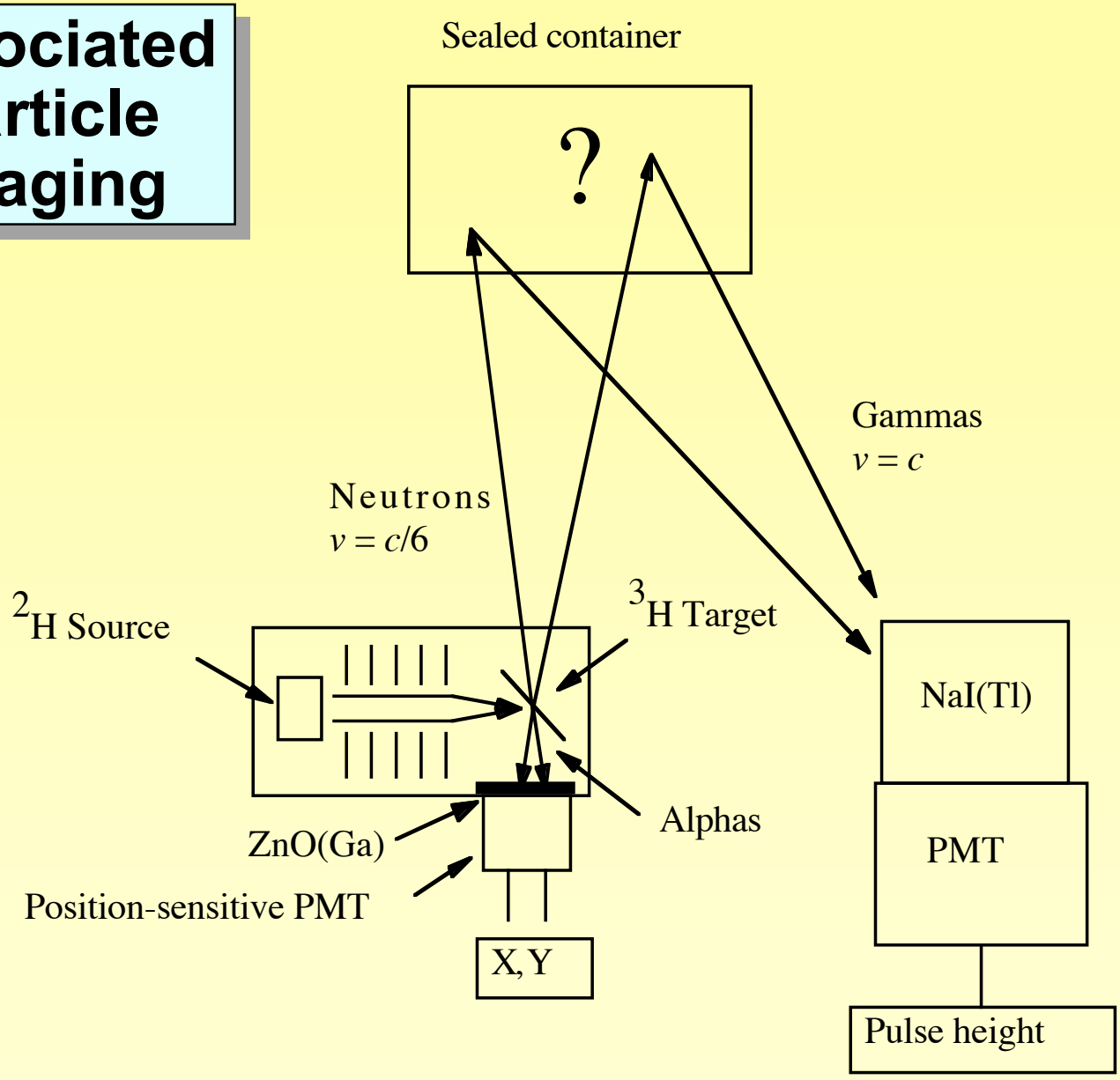
Two Ultra-Fast Semiconductor Scintillators



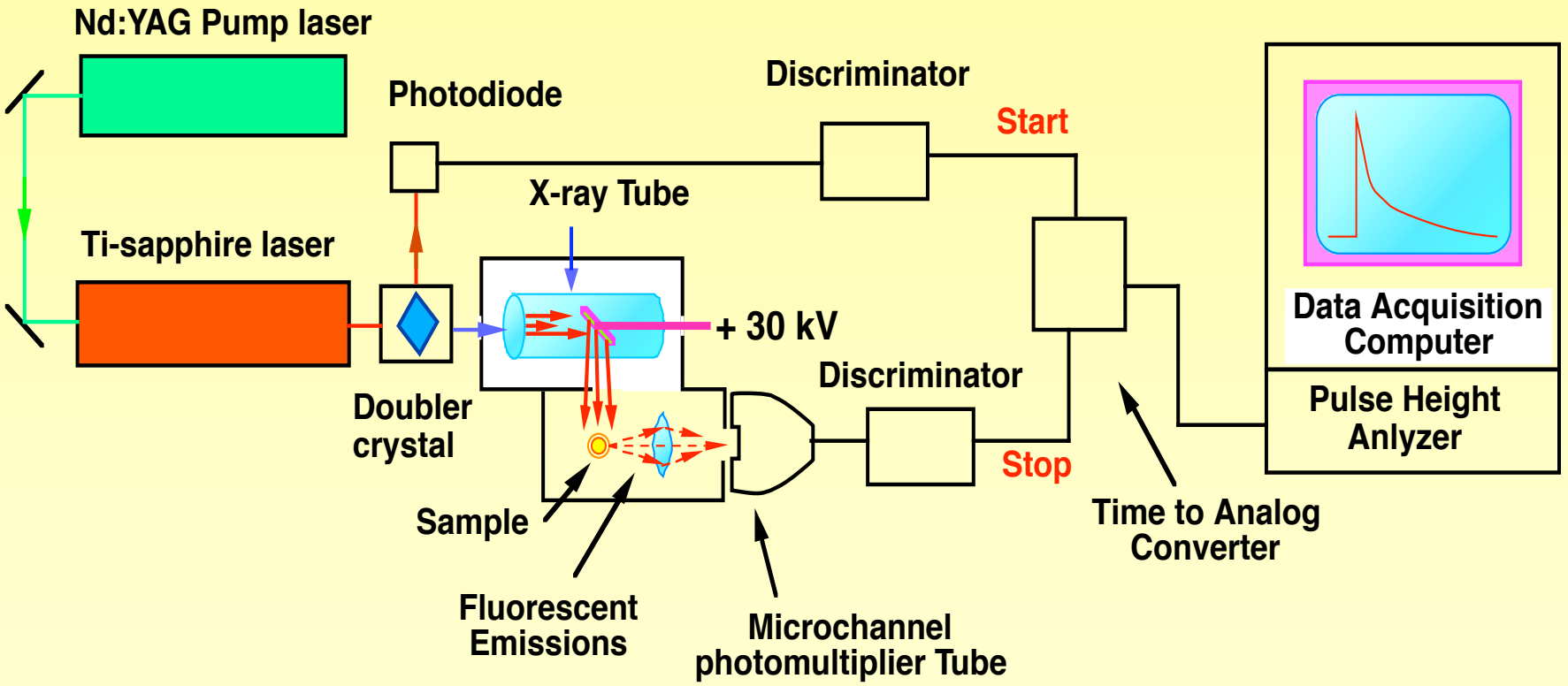
ZnO(Ga)

Material	Efficiency (NaI(Tl)=100%)	Decay Constant (1/e, μsec)	Emission Wavelength (nm)		Index of Refraction	Density (gm/cm³)	Hygroscopic
			Max	Cut Off			
NaI(Tl)	100	0.23	415	320	1.85	3.67	Yes
BaF_2	15	0.6	310	220	1.49	4.88	No
	2-3	0.0008	220	180			
Bi_4GeO_{12}	10-12	0.3	480	350	2.15	7.13	No
$CaF_2(Eu)$	50	0.94	435	405	1.44	3.18	No
$CdWO_4$	18	5/20	540	450	2/2.4	7.9	No
CsF	3-5	0.005	390	250	1.48	4.64	Yes
CsI(Na)	85	0.63	420	300	1.8	4.51	Yes
CsI(Pure)	5-7	0.010	315	250	1.8	4.51	No
CsI(Tl)	45	1.00	565	330	1.8	4.51	No
ZnO(Ga)	38	0.0015	385	350	2.02	5.61	No

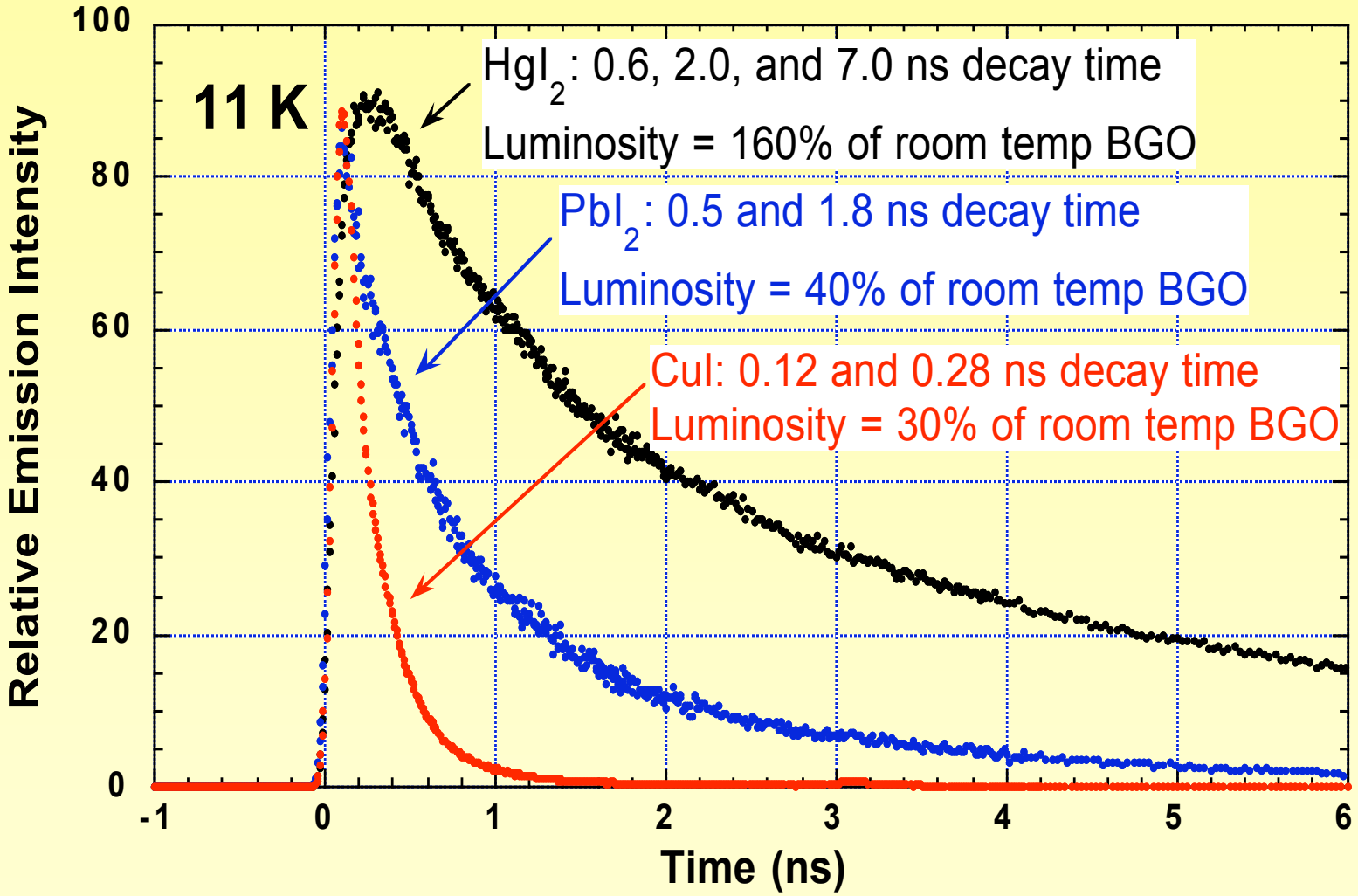
Associated Particle Imaging



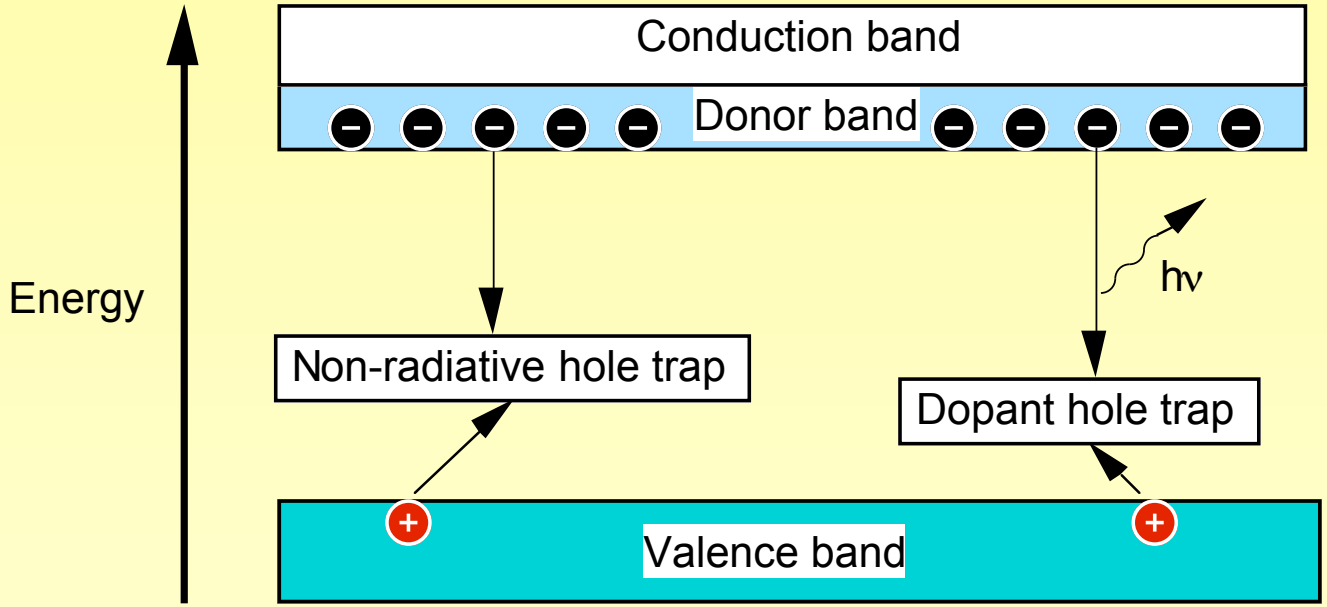
LBNL Pulsed X-Ray Facility



Direct-Gap Semiconductor Scintillators at 11 K

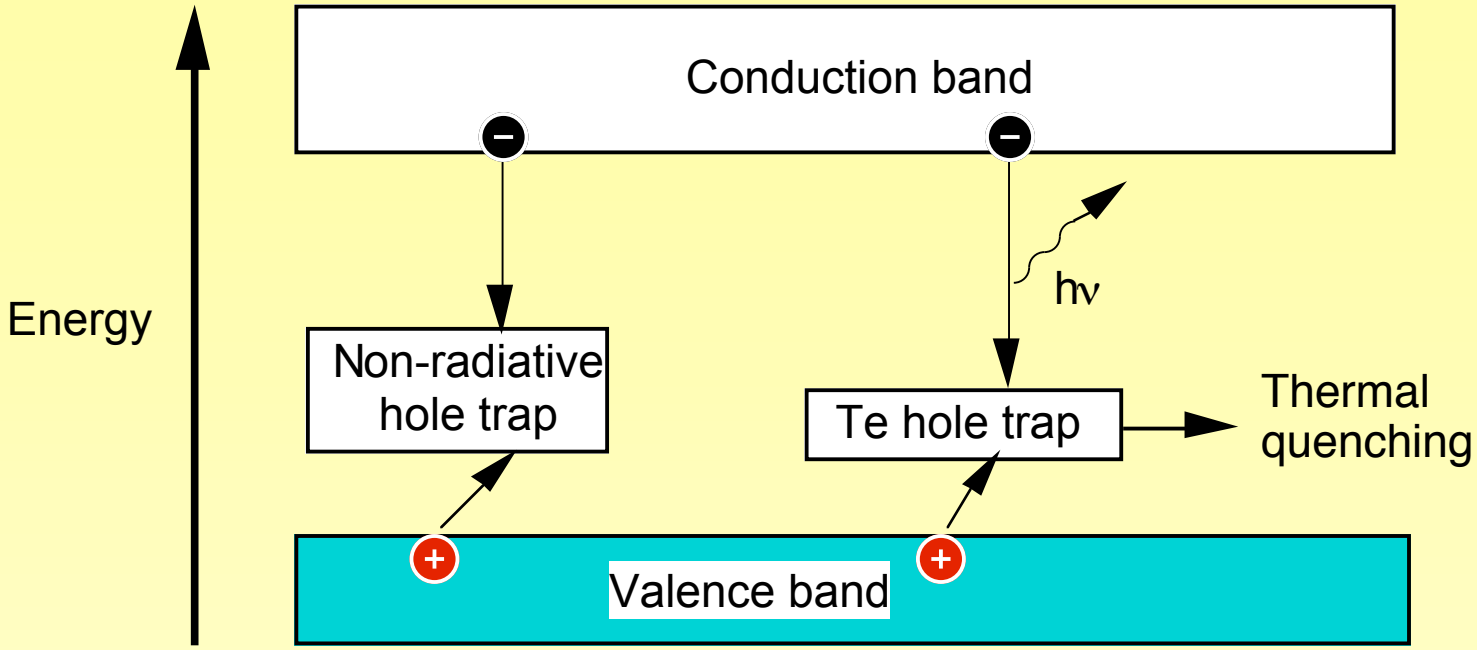


Proposed Ideal Scintillation Mechanism in Codoped Semiconductors



- Direct-gap semiconductor host with E_g = >2.5 eV
- Prompt (<50 ps), efficient trapping of hot holes by dopant ions
- Fast (~1 ns) recombination with donor band electrons

Scintillation from CdS:Te

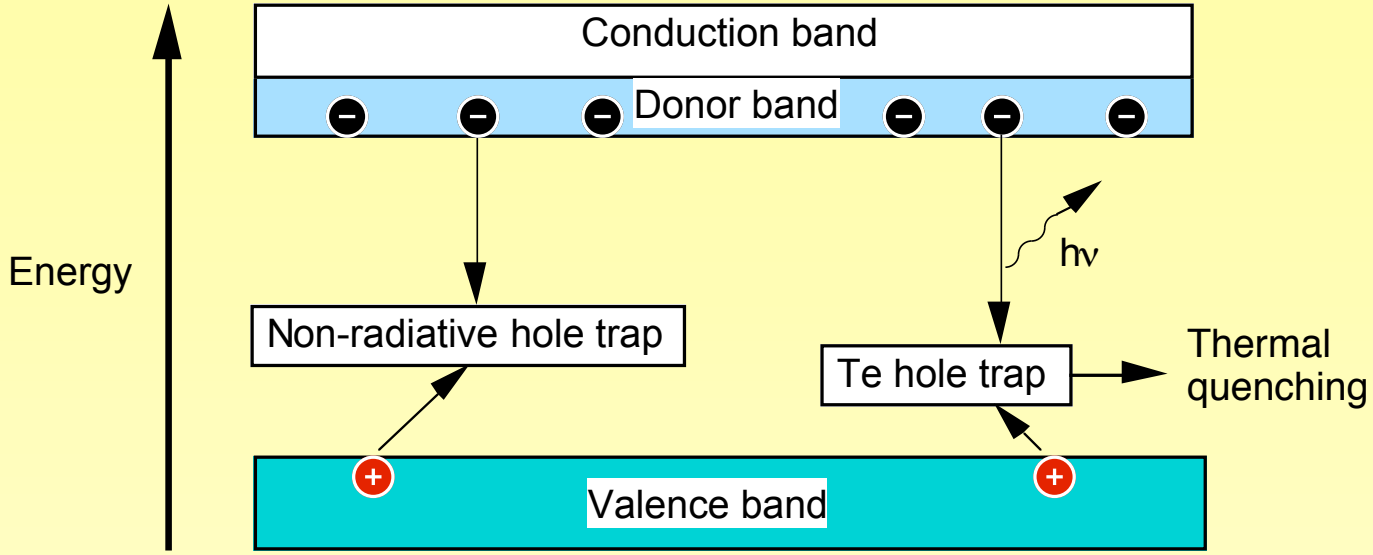


- Tellurium is an isoelectronic hole trap in CdS
- The local hole causes lattice relaxation so the emission is shifted from the band edge (Stoke's shift 512 –> 620 nm, 0.42 eV)

P. Schotanus, P. Dorenbos and V. D. Ryzhikov, "Detection of CdS(Te) and ZnSe(Te) scintillation light with silicon photodiodes," *IEEE Trans Nucl Sci,* vol. NS-39, pp. 546- 550, **1992**.

- Luminosity is 17,000 photons/MeV (2 x BGO)
- 18 ns (1.1%), 270 ns (19%), 3 μs (80%) -complex emission, ascribed to multiple sites and complexes

Scintillation from CdS(In,Te)

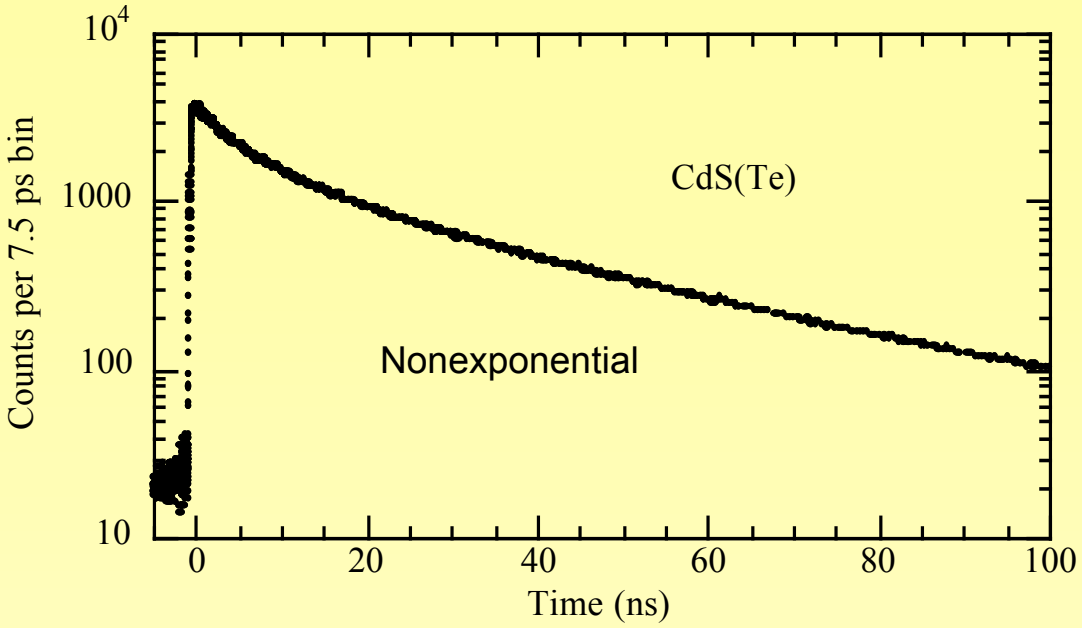


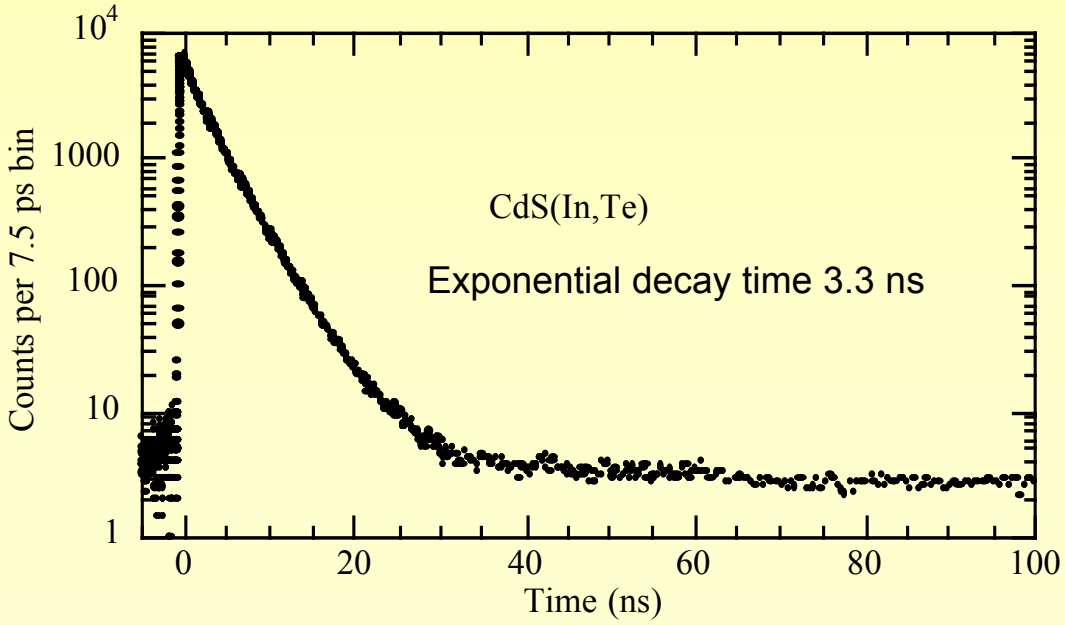
- The indium donor band provides electrons of both spin, so that fast singlet –> singlet radiative recombination is possible
- Tellurium still acts as a hole trap, just as in CdS:Te

Codoped CdS at Room Temperature

Tellurium doping alone results in a slow scintillator (80% τ = 3 μs)

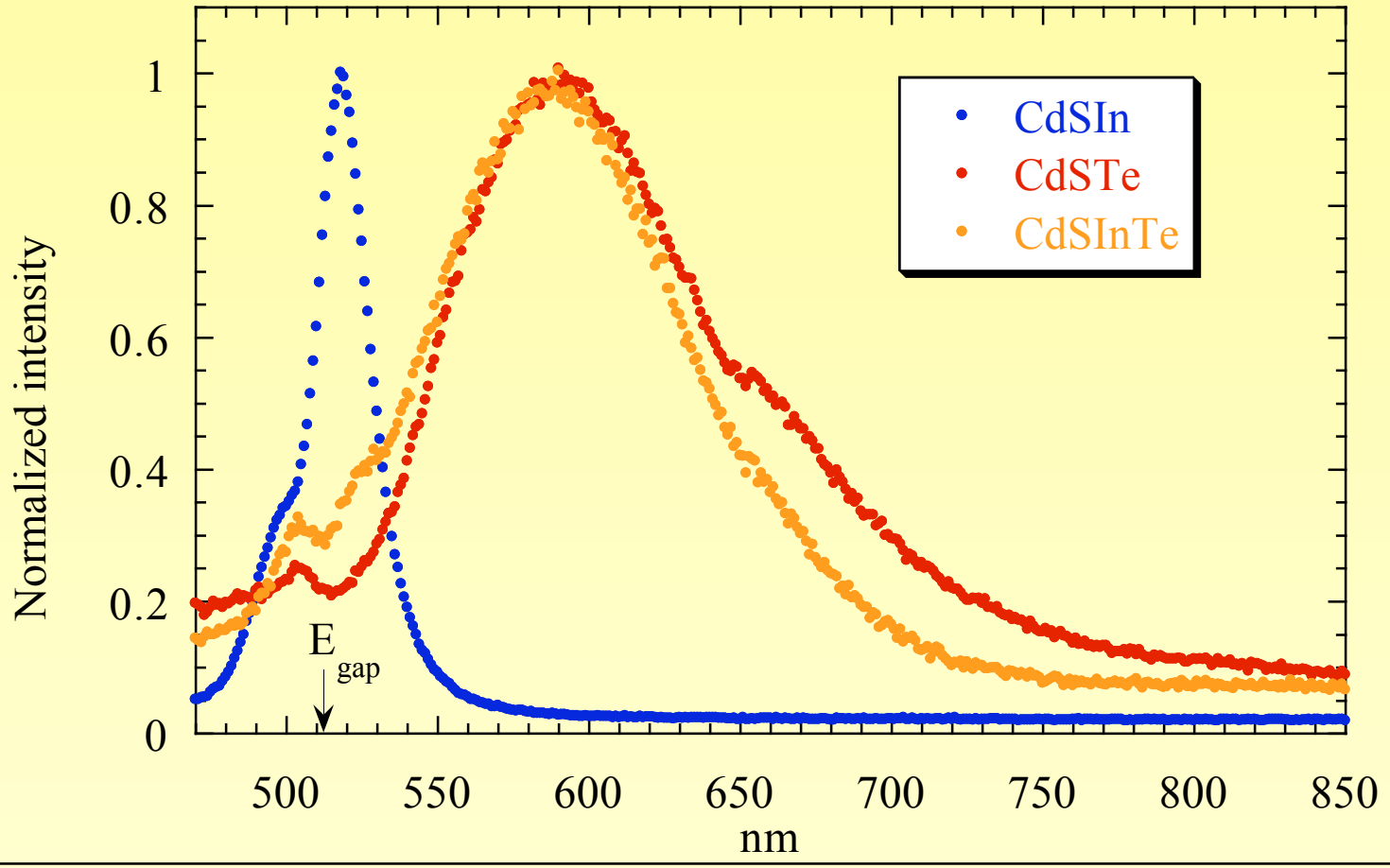
Indium donor band electrons recombine quickly with holes trapped on tellurium (τ = 3.3 ns)





Ernest Orlando Lawrence Berkeley National Laboratory

Room-Temperature Photoluminescence Spectra



CdS:Te,In is the same transition as CdS:Te only much faster

Direct-Gap Semiconductor Scintillator

General selection criteria plus:

- Direct band gap 2.2 to 3.5 eV (≈ 1 ns decay time)
- 5 to 7 eV per electron-hole pair
- Shallow acceptor and donor (near band-edge emission)
- Fundamental limit 200,000 photons/MeV
- Fundamental limit 1.5 % fwhm at 662 keV

Advantages: (1) ultra-fast decay time (2) maximum potential luminosity

Conclusions

- The development of new detector materials has been hindered by the slow pace of empirical discovery
- We need to move from empirical discovery to methods that use
  - The >10,000 heavy-atom crystals in the ICDS whose synthesis and structure is known but are otherwise unexplored
  - First-principle calculations of physical and luminescent properties to help select candidates for synthesis and measurement
  - Stability and growth calculations to optimize crystal growth
  - Powder synthesis and characterization to efficiently screen candidates
- The prizes
  - New heavy-atom semiconductors that are easy to grow as large crystals and have good electron transport
  - New heavy-atom scintillators that are easy to grow in as very large crystals and can be doped to be both bright and fast

Periodic Table

H 1																He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	*Tc* 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	*Po* 84	*At* 85	*Rn* 86

↓

Ce 58	Pr 59	Nd 60	*Pm* 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71

Cluster vs. Periodic Computational Approaches

- Cluster of ions
  - + Ionic crystals
  - + Electronic defects < cluster size (e.g. vacancies, trapped carriers)
  - – Environment of periodic crystal (pt. charges can reproduce crystal field with high accuracy)
  - – Overestimates band gaps
  - – Cannot handle delocalized defects

- Infinite, periodic 3D array of unit cells
  - + Environment of periodic crystal
  - + Covalent crystals
  - + Electronic structure > unit cell
  - – Underestimates band gaps (higher order theory may fix)
  - – Localized defects repeated in all directions