Inorganic Scintillators for the detection of ionizing radiation

P. Dorenbos
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Scintillator applications

- security
- medical diagnostics
- industry + science
- space explorations
- high energy physics
Topics

- How it works?
  - The light output
  - The luminescence
  - The scintillation mechanism
  How many photons are emitted?
  What is color and speed of emission?
  What happens on an atomic scale?

- How it performs?
  - Energy resolution
  - Time resolution
  What is the status and are the limits?
  What is the status and are the limits?

- How it is used?
  - Current developments
  What are the hot topics today?
The scintillation process

Ionizing radiation

$\gamma$-photon
neutron
particle

1MeV

ionization
rack

inorganic compound (crystal) = host lattice

50000 photons

in between a lot is happening!
Schematic of a radiation detector

Alpha
Proton
Electron

X-ray
Gamma-ray

scintillator

Radiation detector

electric signal

photon detector
<table>
<thead>
<tr>
<th>Scintillators</th>
<th>Light sensors</th>
</tr>
</thead>
<tbody>
<tr>
<td>inorganic crystals/powder</td>
<td>Human eye</td>
</tr>
<tr>
<td>organic plastics/crystals</td>
<td>Photomultiplier tubes</td>
</tr>
<tr>
<td>glass</td>
<td>silicon photo diodes</td>
</tr>
<tr>
<td>liquid</td>
<td>Si-PMTs</td>
</tr>
<tr>
<td>gas</td>
<td>CCDs</td>
</tr>
<tr>
<td></td>
<td>gas-filled detectors</td>
</tr>
</tbody>
</table>
The Bolognian stone
History of scintillator discovery

Invention of Photomultiplier tube

Human eye

CaWO₄

1900 1920 1940 1960 1980 2000 2020

LaBr₃:Ce
LaCl₃:Ce
RbGd₂Br₇:Ce
LuAlO₃:Ce
Lu₂SiO₅:Ce
PbWO₄
CeF₃
(Y,Gd)₂O₃:Ce
BaF₂ (fast)
YAlO₃:Ce
Bi₄Ge₃O₁₂
BaF₂ (slow)
CsI:Na
CdS:In
ZnO:Ga
CaF₂:Eu
silicate glass:Ce
LiI:Eu
CsI
CsF
CsI:Tl
CdWO₄
NaI:Tl
PbWO₄
Lu₂SiO₅:Ce
LuAlO₃:Ce
Bi₄Ge₃O₁₂
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ZnO:Ga
CaF₂:Eu
silicate glass:Ce
LiI:Eu
CsI
CsF
CsI:Tl
CdWO₄
NaI:Tl
History of scintillator discovery

TU-Delft discoveries
Main drivers of scintillation research

- Homeland security
  - High resolution scintillators for radioisotope identification
  - Shortage of $^3$He→thermal neutron scintillators
- Space explorations
  - High resolution, low intrinsic count rate scintillators
- Medical diagnostics
  - TOF-PET very fast risetime scintillators
  - SPECT
- High energy physics
  - High density and high radiation hardness
  - Large volumes at low cost
Important gamma ray scintillator parameters

- High light output: \( Y \) (photons/MeV)
- Fast scintillation speed: \( \tau_s \) (ns)
- Low energy resolution: \( R_{\text{FWHM}} \) (%)
- High density for \( \gamma \) detection: \( \rho \) (g/cm\(^3\))
- Large size of crystal: 10-100-1000 cm\(^3\)
- Low cost per cm\(^3\)
- Low afterglow (low phosphorescence)
- Low background count rate (low intrinsic activity)
  - Absence of radioactive isotopes

Importance depends on application
## Properties of inorganic scintillators

<table>
<thead>
<tr>
<th>scintillator</th>
<th>$\rho$</th>
<th>$n$</th>
<th>$\tau$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$N_{\text{phot}}/\text{MeV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaI (at 80 K)</td>
<td>3.67</td>
<td>1.75</td>
<td>60</td>
<td>303</td>
<td>76000</td>
</tr>
<tr>
<td>NaI (Tl)</td>
<td>3.67</td>
<td>1.75</td>
<td>230</td>
<td>415</td>
<td>38000</td>
</tr>
<tr>
<td>CsI (Tl)</td>
<td>4.51</td>
<td>1.75</td>
<td>3340</td>
<td>540</td>
<td>65000</td>
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<tr>
<td>BaF$_2$</td>
<td>4.89</td>
<td>1.5</td>
<td>630</td>
<td>310</td>
<td>9500</td>
</tr>
<tr>
<td>(valence $e^- to core$)</td>
<td></td>
<td></td>
<td>0.6</td>
<td>220</td>
<td>1400</td>
</tr>
<tr>
<td>Bi$_4$Ge$<em>3$O$</em>{12}$ (BGO)</td>
<td>7.13</td>
<td>2.15</td>
<td>300</td>
<td>480</td>
<td>8200</td>
</tr>
<tr>
<td>PbWO$_4$</td>
<td>8.28</td>
<td>2.20</td>
<td>10</td>
<td>470</td>
<td>100</td>
</tr>
<tr>
<td>Lu$_2$SiO$_5$:Ce (LSO)</td>
<td>7.4</td>
<td>1.8</td>
<td>47</td>
<td>420</td>
<td>25000</td>
</tr>
<tr>
<td>YAIO$_3$:Ce (YAP)</td>
<td>5.37</td>
<td>1.95</td>
<td>27</td>
<td>370</td>
<td>18000</td>
</tr>
<tr>
<td>LaCl$_3$:Ce</td>
<td>3.7</td>
<td>1.8</td>
<td>35</td>
<td>350</td>
<td>50000</td>
</tr>
<tr>
<td>LaBr$_3$:Ce</td>
<td>5.1</td>
<td>2.1</td>
<td>17</td>
<td>380</td>
<td>70000</td>
</tr>
</tbody>
</table>
The growth of NaI:Ti scintillation crystals

dr. A. Gektin and prof. C.W.E. van Eijk with a NaI:Ti ingot
Examples or bare scintillation crystals

CsI (Tl)

NaI (Tl)

CdWO₄

BGO
Examples of packed crystals

**Gamma camera crystal**

**NaI(Tl) crystals**

7 to 61 photomultipliers

**NaI:Ti⁺ crystal** 20-60 cm diameter and 2-25 mm thick
The scintillation process

Ionizing radiation

$\gamma$-photon, neutron, particle

Inorganic compound (crystal) = host lattice

Ionization track

Luminescence Centre

Photon flash

1 MeV → 50,000 photons

What is happening in between? A lot!
The scintillation process

Three phases
1. The interaction phase + thermalization phase (ps)
2. The charge carrier and energy migration phase (ps-ns-ms)
3. The luminescence phase (ns-μs)

\[ E_g = 3-10 \text{ eV} \]

- VIS 400 - 800 nm 3.1 - 1.6 eV
- UV 180 - 400 nm 6.9 - 3.1 eV
- VUV < 180 nm > 6.9 eV
Phase I: The interaction phase

- Gamma ray interaction $\rightarrow$ energetic electron
  - The photo-electric effect
  - The Compton scattering
  - Pair production

$Z_{eff}^{3-4}$ (dominant $<100$ keV)
$\rho$ (dominant around 1 MeV)
$E_\gamma > 1.02$ MeV

- $Z(I) = 53$
- $Z(Cs) = 55$
- $Z(La) = 57$
- $Z(Gd) = 64$
- $Z(Lu) = 71$
- $Z(Pb) = 82$
- $Z(Bi) = 83$
The ionization track in scintillators

- 10 keV – 10 MeV X-ray or gamma-rays produce fast primary electrons

The Bethe formula

\[-\frac{dE}{dx} = \frac{4\pi e^4 z^2}{m_0 v^2} NZ \left[ \ln \left( \frac{2m_0 v^2}{I} \right) - \ln \left( 1 - \frac{v^2}{c^2} \right) - \frac{v^2}{c^2} \right] \]

\( e_z \) = particle charge
\( v \) = particle velocity
\( N, Z \) = number density and atomic number atoms
\( I \) = average ionization potential atoms

Smaller energy \( \rightarrow \) smaller \( v \) \( \rightarrow \) higher \( \frac{dE}{dx} \) \( \rightarrow \) more ionizations/volume
• Multiple interactions
  • One scintillation event can produce separate ionization tracks in the scintillator
  • Everything takes place in the 1-10 ps time scale
  • Separate flashes add to one scintillation flash
• High energy physics GeV-TeV→ shower of events
Energy needed for electron-hole pair generation

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>Z</th>
<th>$E_g$ (eV)</th>
<th>$E_{ion}$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>2.33</td>
<td>14</td>
<td>1.12</td>
<td>3.6</td>
</tr>
<tr>
<td>Ge</td>
<td>5.33</td>
<td>32</td>
<td>0.67</td>
<td>2.9</td>
</tr>
<tr>
<td>GaSe</td>
<td>4.55</td>
<td>31, 34</td>
<td>2.03</td>
<td>4.5</td>
</tr>
<tr>
<td>InP</td>
<td>4.78</td>
<td>49, 15</td>
<td>1.30</td>
<td>4.2</td>
</tr>
<tr>
<td>CdS</td>
<td>4.84</td>
<td>48, 16</td>
<td>2.60</td>
<td>7.3</td>
</tr>
<tr>
<td>GaAs</td>
<td>5.32</td>
<td>31, 33</td>
<td>1.43</td>
<td>4.3</td>
</tr>
<tr>
<td>InSb</td>
<td>5.77</td>
<td>49, 51</td>
<td>0.20</td>
<td>0.6</td>
</tr>
<tr>
<td>CdSe</td>
<td>5.80</td>
<td>48, 34</td>
<td>1.73</td>
<td>5.5</td>
</tr>
<tr>
<td>CdTe</td>
<td>6.20</td>
<td>48, 52</td>
<td>1.44</td>
<td>4.7</td>
</tr>
<tr>
<td>PbI$_2$</td>
<td>6.20</td>
<td>82, 53</td>
<td>2.55</td>
<td>7.7</td>
</tr>
<tr>
<td>HgI$_2$</td>
<td>6.40</td>
<td>80, 53</td>
<td>2.13</td>
<td>4.2</td>
</tr>
<tr>
<td>TlBr</td>
<td>7.56</td>
<td>81, 35</td>
<td>2.68</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Figure 13.21: The average energy required to form one electron–hole pair (e) versus bandgap energy for a number of semiconductor materials. (From Klein.45)
The ionization track and electron-hole creation

\[ N_{eh} = \frac{E_\gamma}{E_{ion}} = \frac{E_\gamma}{\beta E_g} \]

\[ \beta \approx 2.5 \]

\[ E_g = 8 \text{ eV} \]

\[ \Rightarrow N_{eh} = 50.000 /\text{MeV} \]

- S is the transfer efficiency from track to luminescence center
- Q is quantum efficiency of luminescence center
The ideal scintillator has $S=Q=1$
Latest developments in scintillation research

Latest materials developments
- Elpasolites (Radiation Monitoring Devices, dr. K. Shah)
- Eu$^{2+}$ doped halides (University of Berkeley, prof. Derenzo, prof. Moses)
- Lu$_3$Al$_5$O$_{12}$:Pr$^{3+}$ (Tohuku Univ, prof. Yoshikawa, Inst. of Phys. Prague, dr. M. Nikl)
Current developments SrI$_2$:Eu

Current developments $\text{Ba}_2\text{CsI}_5:\text{Eu}^{2+}$

Fig. 1. A 1 cm in diameter $\text{Ba}_2\text{CsI}_5:\text{Eu}^{2+}$ shown as-grown in a sealed quartz ampoule.

Fig. 3. Pulse height spectra of $\text{Ba}_2\text{CsI}_5:\text{Eu}^{2+}$ and NaI:Tl measured under $^{137}\text{Cs}$ gamma-ray excitation.

Current developments $\text{BaBrI}_3:\text{Eu}^{2+}$

Recently more materials were discovered. All have their pros and cons.

<table>
<thead>
<tr>
<th>Scintillators</th>
<th>Pr:LuAG (Lu₃Al₅O₁₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>6.7</td>
</tr>
<tr>
<td>Light Yield (BGO=100)</td>
<td>330</td>
</tr>
<tr>
<td>Decay Time (ns)</td>
<td>&lt;25</td>
</tr>
<tr>
<td>Peak emission (nm)</td>
<td>310</td>
</tr>
<tr>
<td>Energy Resolution (%@662keV)</td>
<td>5</td>
</tr>
<tr>
<td>Hygroscopicity</td>
<td>No</td>
</tr>
<tr>
<td>Cleavage</td>
<td>No</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>1970</td>
</tr>
</tbody>
</table>

Fast and good energy resolution
But high intrinsic background (Lu)
The scintillation process; phase III

Three phases
1. The interaction phase + thermalization (ps)
2. The charge carrier and energy migration phase (ns-ms)
3. The luminescence phase (ns-μs)

E_g = 3-10 eV

Valence band
Cond. band

S

Q

photon

Ideal scintillator
S = Q = 1
The luminescence phase

The most popular activator ions

- The $6s^2$-ions $\text{Tl}^+$, $\text{Pb}^{2+}$, $\text{Bi}^{3+}$
  - NaI:Tl, CsI:Tl, $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, PbWO$_4$

- The lanthanide ions $\text{Ce}^{3+}$, $\text{Pr}^{3+}$, $\text{Eu}^{2+}$
  - $\text{YAlO}_3$:Ce, $\text{Y}_3\text{Al}_5\text{O}_{12}$:Ce, $\text{Lu}_2\text{Si}_5\text{O}_5$:Ce, $\text{LuAlO}_3$:Ce, $\text{LaCl}_3$:Ce, $\text{LaBr}_3$:Ce, $\text{LiI}$:Eu, $\text{Lu}_3\text{Al}_5\text{O}_{12}$:Pr$^{3+}$
6s$^2$-ions Tl$^+$, Pb$^{2+}$, Bi$^{3+}$

- **Ground state configuration**: 6s$^2$
- **Excited state configuration**: 6s6p

**Selection rules**

- Allowed transitions:
  - $\Delta J = 0, \pm 1$ (not $J = 0 \rightarrow J' = 0$), $\Delta S = 0$

- Singlet $\rightarrow$ singlet: allowed, fast
- Triplet $\rightarrow$ singlet: forbidden, slow

**Relaxation**

- NaI: Tl: $\tau = 230$ ns
- CsI: Tl: $\tau = 3.3$ $\mu$s
Lanthanide luminescence

- Electron configuration: \([\text{Xe}]4f^n5d^0\)

- 4f electrons are shielded from the crystalline field. Level energies independent on host lattice.

- 5d electron strong interaction with crystal field. Level energies depend on host crystal.
The Dieke diagram of free ion trivalent lanthanide $4f^n$ and $5d$ levels.
The emission wavelength

• Electrons either in the ground state or excited state of a luminescence center interact with the surrounding atoms in a compound
  • 4f electrons have negligible interaction
  • 5d electrons (also 6s and 6p electrons of 6s²-ions) have strong interaction

• Interaction depends on
  • Crystal structure,
    • coordination number, bond lengths etc.
  • The chemical properties of the anions
    • F⁻, Cl⁻, Br⁻, I⁻ and O²⁻, S²⁻

• The emission of Ce³⁺ may vary from 300 nm in fluoride compounds up to 600 nm in sulfide compounds
Characteristic emission spectra Ce, Pr, Nd

- Ce: Lu$_2$S$_3$, LiF$_4$
- Pr: Y$_5$Al$_5$O$_{12}$, LiLuF$_4$
- Nd: LaF$_3$

Wavelength [nm]:

- Ce: 800, 600, 400, 200
- Pr: 1400, 1200, 1000, 800
- Nd: 1000, 800, 600, 400

Wavenumber [10$^3$ cm$^{-1}$]:

- Ce: 10, 20, 30, 40, 50, 60
- Pr: 10, 20, 30, 40, 50, 60
- Nd: 10, 20, 30, 40, 50, 60

Emission transitions:

- 4f$^2$ → 4f$^2$
- 4f$^3$ → 4f$^3$

Yield [arb. units]:

- Ce, Pr, Nd: 0.4, 0.8

Energy [eV]:

- Ce, Pr, Nd: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12
Emission and quantum efficiency

![Graph showing emission and quantum efficiency](image)

- **Emission and Quantum Efficiency**
  - **Photomultiplier tube**
  - **Silicon Photodiode**
  - **Yield [arb. units]**
  - **Wavelength [nm]**
  - **Wavenumber [10^3 cm⁻¹]**
Ce$^{3+}$ doped lanthanide compounds are ideal for gamma ray scintillators

- Fast dipole and spin allowed 5d-4f emission (15-60 ns)
- Emission wavelength matches sensitivity of photomultiplier tubes
- High thermal stability of emission
- Absence of slow 4f-4f emission
- Ce$^{3+}$ is a good hole trap which is regarded as a first important step in the scintillation process
- Lanthanide (La, Gd, Lu) based host lattices are dense providing efficient gamma ray detection materials
  - LaBr$_3$:Ce, Gd$_2$SiO$_5$:Ce, Lu$_2$SiO$_5$:Ce
Stokes shift and self-absorption

- A scintillator crystal needs to be transparent to its own scintillation light
- A photon emitted by a luminescence center can be re-absorbed by another luminescence center of the same type
- Probability increases with:
  - Larger activator concentration
  - Higher temperature (broadening of emission and absorption bands)
  - Larger crystal size
  - Smaller value for the Stokes shift
- Stokes shift = energy difference between emission and first absorption band of luminescence center
Stokes shift and self-absorption

Stokes shift is the energy lost due to lattice relaxation.
Aspects of self-absorption in LaBr$_3$:5% Ce

- High energy part of emission re-absorbed by Ce$^{3+}$
- Re-emission by Ce$^{3+}$
  - emission profile changes
  - scintillation decay time lengthening
  - scintillation light losses (because Q<1)
Thermal quenching

Important for:
- luminescence efficiency $Q$
- stable scintillator operation against temperature fluctuations
- high temperature applications e.g. oil-well logging
Thermal quenching of luminescence

Configuration coordinate

Energy $E$

$0.1 \text{ fs}$

$1 \text{ ps}$

$> \text{ ns}$

Conduction band states

Configuration coordinate

Energy $E$

$0.1 \text{ fs}$

$> \text{ ns}$

$\Gamma_T = \frac{\Gamma_v}{\Gamma_v + \Gamma_q}$

$\tau(T) = \frac{\tau_v^{-1}}{\tau_v^{-1} + s_0 \exp \frac{-\Delta E_q}{k_B T}}$
Thermal quenching of Ce\textsuperscript{3+} emission

If quenching via CB-states than 5d-level location important
So far we have treated:

• **Phase I**: Interaction of a gamma photon with scintillators
  • Creation of the ionization track
  • Relation between number of ionizations and band gap

• **Phase III**: The luminescence centers
  • $s^2$-elements (Tl, Pb, Bi) and lanthanides ($\text{Ce}^{3+}$, $\text{Pr}^{3+}$)
  • Wavelength of emission, self-absorption, Stokes shift
  • Thermal stability and thermal quenching

• **Next, Phase II**: scintillation mechanisms
  • Intrinsic scintillators
    • Self trapped exciton and core valence luminescence
  • Activated scintillators
    • energy migration from ionization track to luminescence centers
    • $\text{LaCl}_3$:Ce and $\text{LaBr}_3$:Ce as an example
Core valence luminescence

condition for CVL: $E_{vc} < E_g$
Self trapped exciton and Core valence luminescence in BaF$_2$

N.N. Ershov, N.G. Zakharov, P.A. Rodnyi

CVL: 1400 ph/MeV  800 ps
STE: $10^4$ ph/MeV  600 ns
What is a self trapped exciton?

- hole in valence band is shared between two anions forming an $X_2^-$ molecule like defect ($V_k$ center)
- electron in an orbit around the $V_k$ center
Scintillation mechanism in LaCl$_3$ and LaBr$_3$

Ce$^{3+}$ + h $\rightarrow$ Ce$^{4+}$
Ce$^{4+}$ + e $\rightarrow$ (Ce$^{3+}$)* $\rightarrow$ photon
17 ns fast scintillation component

e + h $\rightarrow$ exciton $\rightarrow$ STE
STE $\rightarrow$ STE emission (or loss)
μs slow scintillation component
STE $\rightarrow$ Ce transfer
X-ray excited luminescence LaCl$_3$:0.6% Ce$^{3+}$

Competition STE emission and Ce emission as function of temperature

**Graph Details:**
- **Wavelength (nm):** 150, 200, 250, 300, 350, 400
- **Temperature (K):** 135, 175, 200, 225, 250, 275, 300, 325, 350, 375, 400
- **Relative Intensity (%):** 0, 20, 40, 60, 80, 100
- **Graph Labels:**
  - **Total**
  - **STE**
  - **Ce$^{3+}$**

**Graph Description:**
- The graph shows the competition between STE emission and Ce emission as a function of temperature.
- The STE emission wavelength is indicated by a red line.
- The graph includes data points for different temperatures, showing the variation in relative intensity.
Competition STE emission and Ce emission as a function of temperature and concentration

a) LaCl₃ 0.6 % Ce

b) LaCl₃ 4 % Ce

c) LaCl₃ 10 % Ce
Summary scintillation processes in La-halides

- Direct capture of electron and holes
  - Fast Ce$^{3+}$ emission decay component of 16 ns
- Creation of self trapped excitons
  - Slow STE emission
  - Thermally activated STE migration
- Energy transfer from STE to Ce$^{3+}$
  - Slow Ce$^{3+}$ scintillation components

Different competing scintillation processes depending on
- Ce concentration
- on temperatures

LaBr$_3$:Ce$^{3+}$; record low energy resolution at 662 keV

Nal:Tl$^+$
- Density: 3.6 g/cm$^3$
- Time: 230 ns
- Resolution: 6.5 %
- Yield: 40000 ph/ MeV

LaBr$_3$:Ce$^{3+}$
- Density: 5.1 g/cm$^3$
- Time: 17 ns
- Resolution: 2.9 %
- Yield: 70000 ph/ MeV
Anatomy of a pulse height spectrum from $^{24}\text{Na}$-source measured with LaBr$_3$:5%Ce

- Photoelectric interaction $\rightarrow$ Total absorption peaks
- Compton scattering $\rightarrow$ Compton edges $\rightarrow$ Compton continua

$$E_C = \frac{2E_\gamma^2}{511 + 2E_\gamma} = 2.52 \text{ and } 1.16 \text{ MeV}$$

spectrum due to 1.37 MeV + 2.75 MeV gamma source
Anatomy of a pulse height spectrum from $^{24}$Na-source measured with LaBr$_3$:5%Ce

- **Pair creation**
  - $e^- + e^+ + E_{\text{kin}} (= E_{\gamma} - 1.02 \text{ MeV})$
  - $e^+ + e^- \rightarrow 2 \times 511 \text{ keV } \gamma \text{ photons}$

- **511 keV escape peak at 2.24 MeV**
- **Double escape at 1.73 MeV**

- **Compton scattering of annihilation quanta with escape of scattered gamma photons**
Anatomy of a pulse height spectrum from $^{24}$Na-source measured with LaBr$_3$:5%Ce

Two remaining features at 511 keV and around 250 keV

Back scatter peaks due to gamma rays scattered from materials outside the scintillator
- Compton scattered gamma’s
- annihilation gamma 511 keV
BrilLanCe™ trademark of La-halide scintillators

Discovered by TU-Delft
LaCl$_3$:Ce crystal growth progress
From labsize to 4”x6” scintillators crystals

Brilliance 350
Scintillation Material

TU Delft
LaBr₃:Ce for nuclide identification

SAM Revealer

The LaBr₃ Advantage

- Analysis Mode
- Easy Search
- GPS Event Stamping
- Multiple Isotopes in Real Time
Comparison NaI:Tl, LaBr₃:Ce, HP-Ge

![Graph comparing count rate vs. energy for NaI, LaBr₃, and HPGe.](image)

<table>
<thead>
<tr>
<th>Real energy [keV]</th>
<th>Element</th>
</tr>
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<tbody>
<tr>
<td>511</td>
<td>annihilation peak</td>
</tr>
<tr>
<td>518</td>
<td>Cl</td>
</tr>
<tr>
<td>583.1</td>
<td>²⁰⁸Tl</td>
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<tr>
<td>788</td>
<td>Ge</td>
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<tr>
<td>911.1</td>
<td>²²⁸Ac</td>
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<td>1165</td>
<td>Cl</td>
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<tr>
<td>1201</td>
<td>H d</td>
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<tr>
<td>1460</td>
<td>⁴⁰K decay</td>
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<tr>
<td>1600</td>
<td>Cl f</td>
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<tr>
<td>1686</td>
<td>Na s</td>
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<td>1712</td>
<td>H s</td>
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<td>1778</td>
<td>Al f</td>
</tr>
<tr>
<td>1953</td>
<td>Cl d</td>
</tr>
<tr>
<td>1957</td>
<td>Cl f</td>
</tr>
<tr>
<td>2223</td>
<td>H</td>
</tr>
<tr>
<td>2611</td>
<td>²⁰⁸Tl</td>
</tr>
<tr>
<td>2622</td>
<td>Na d</td>
</tr>
<tr>
<td>2676</td>
<td>Cl f</td>
</tr>
<tr>
<td>2843</td>
<td>Si d</td>
</tr>
<tr>
<td>2864</td>
<td>Cl f</td>
</tr>
<tr>
<td>2977</td>
<td>F s</td>
</tr>
<tr>
<td>2997</td>
<td>Cl f</td>
</tr>
<tr>
<td>3017</td>
<td>F f</td>
</tr>
<tr>
<td>3062</td>
<td>Cl f</td>
</tr>
</tbody>
</table>
LaBr$_3$:Ce in 2011 on mission to Phobos (Mars) and in 2014 on mission to Mercury.

LaBr$_3$ detector for the Phobos-Grunt mission.

LaBr$_3$ detector for the BepiColombo mission.
Aspects that determine resolution

\[ R^2 = R_{\text{stat}}^2 + R_{\text{inhom}}^2 + R_{\text{nonprop}}^2 \]

\[ R_{\text{stat}}^{\text{FWHM}} (\%) = 235 \sqrt{\frac{1 + v_{\text{PMT}}}{N_{\text{dph}}}} \quad v_{\text{PMT}} \approx 0.2 \]

• the fundamental limit is governed by statistics
• you need to detect as many photons as possible
  → bright scintillator
  → efficient low noise photon detector
The ideal scintillator has $S=Q=1$
Energy resolution @ 662 keV

- $R_{\text{stat}} = 2.35 \sqrt{1 + 0.2 \frac{1}{N_{dph}}}$

- YAlO$_3$:Ce, Lu$_3$Al$_5$O$_{12}$:Pr, LaCl$_3$:Ce, LaBr$_3$:Ce, SrI$_2$:Eu are reasonably close to fundamental limit.
- Lu$_2$SiO$_5$, NaI:Tl, CsI:Tl, strong deviation

What causes the strong deviation?
Aspects that determine resolution

\[ R^2 = R_{\text{stat}}^2 + R_{\text{inhom}}^2 + R_{\text{nonprop}}^2 \]

\[ R_{\text{stat}}^{\text{FWHM}} \% = 235 \sqrt{\frac{1 + \nu_{\text{PMT}}}{N_{\text{dph}}}} \quad \nu_{\text{PMT}} \approx 0.2 \]

- when the number of created photons is not proportional with the energy of the primary electron
  \( \rightarrow \) additional contribution to resolution (\( R_{\text{nonprop}} \))
- topic of current interest
  \( \rightarrow \) for study, we need a tunable \( \beta \)-source inside scintillator!
The Compton Coincidence Technique

- Developed by Valentine and Rooney
- Provides electron response curves

\[
\begin{align*}
hv' &= \frac{hv}{1 + \left(\frac{hv}{m_0c^2}\right)\left(1 - \cos \theta\right)} \\
E_C &= hv - hv'
\end{align*}
\]

Advantage
- intrinsic tunable β-source
- energy range 6-400 keV

Fig. 1. Block diagram of Compton Coincidence Technique (CCT).
Scintillator response to electrons


- NaI:Ti, LSO:Ce - Strongly Non-proportional
- LaBr₃:Ce, LaCl₃:Ce, YAlO₃:Ce - Proportional
K-dip spectroscopy method

\[ E_{\text{phe}} = E_X - E_K = \Delta E \]

\[ E_X = E_K + \Delta E \]

Energy photo-electron = \( E_X - E \) keV

Yield (photo-electron) = total yield - yield@\( E_K \) keV

→ We have created a tunable internal β-source

→ Electron response from ~0.1 to \((100 - E_K)\) keV
Tunable synchrotron X-ray source

- Synchrotron X-ray beamline HASYLAB, DESY, Hamburg
- 9-100 keV monochromatic and tunable
  - 5-15 eV energy resolution
- Pencil beam
  - → we always excite the same volume element of the scintillator
  - → minimum contribution to resolution from scintillator inhomogeneity
Joining K-dip with SLYNCI data
→ 100eV – 400keV
→ Electron response curves
→ 20 different scintillators
Can we go below 2% energy resolution at 662 keV?

- We need bright scintillators combined with low noise photon detectors
- We need proportional scintillators
Time resolution

Time resolution = accuracy with which the moment of interaction can be determined

It depends:
- scintillation speed (decay time and rise time)
  - more ph/MeV
- photon detector time resolution
- electronics
Timing resolution

The steepness of the rising pulse is important.

BaF$_2$

STE

0.6 $\mu$s

fast

780 ps

LaBr$_3$:0.5% Ce

230 ns

LaBr$_3$:4% Ce

17 ns

NaI:Tl

230 ns

LaBr$_3$:0.5% Ce

230 ns

Nal:Tl

230 ns

FIGURE 3. Decay of the scintillation emission of Nal(Tl), BGO, and LSO(Ce), after excitation by $\gamma$-rays.
Scintillator risetime studies

Photon counts

[Graph showing photon counts over time for different materials]

- \( \text{CaGa}_2\text{S}_4: \text{Ce}^{3+} \) [host excited]
- \( \text{LSO:Ce}^{3+} \) [5d excited]

Time [picosecond]

- fs laser excitation
- Pulsed X-ray excitation
- \( \text{LaBr}_3: \text{Ce} \)
Fast timing is important for
- positron emission tomography
- positron life time studies
- time of flight applications

Typical numbers for time resolution with PMTs and 1 MeV gamma’s:

- NaI(Tl): 1 ns
- BGO: 2-4 ns
- BaF$_2$: 200 ps
- Plastics: 150 ps

Time resolution LaBr$_3$:Ce at 511 keV with PMTs
LaBr$_3$ TOF-PET scanner

Time-of-flight positron emission tomography scanner
- 511 keV annihilation photons
- Coincident detection
- Time resolution 200 ps

Contains 38,880 LaBr$_3$ crystals

First prototype LaBr$_3$ TOF-PET-scanner (2008-2009)
(dr. J. Karp Pennsylvanian State University)
(and Philips Medical Systems)
First TOF PET-image with LaBr$_3$:Ce (October 2009)

Advantage TOF-PET strong false signal reduction especially important For fat patients
Timing Spectra with SiPM – CRT at Optimum Threshold Settings

LaBr$_3$:5% Ce

LYSO

Data Gaussian Fit

FWHM = 100 ps

FWHM = 172 ps
With abundance of 2.6% $^{176}\text{Lu}$ with half life of $3.8 \times 10^{10}$ years an intrinsic activity of 290 cnts/cm$^3$ is obtained.

$^{176}\text{Lu}$ isotopes emit 89, 202, plus 307 keV $\gamma$-photons plus emission of a $\beta^-$ with maximum energy of 596 keV (plus a neutrino).
Intrinsic activity of LaBr$_3$:Ce

With abundance of 0.089% $^{138}$La with half life of 1.0x10$^{11}$ years an intrinsic activity of 1.4 cnts/cm$^3$ is obtained.

$^{138}$La emits either a 1.436 MeV gamma plus an 32 keV X-ray from Ba or it emits a $\beta^-$ with $E_{\text{max}} = 255$ keV plus a 789 keV gamma.
Final remarks

• Ideal scintillator does not exist
  • compromise based on the application
• High resolution for spectroscopy (isotope identification)
  • proportional scintillators
• extremely fast rise time for timing and TOF applications
• low intrinsic count rate for space explorations
• hight density at low cost
  • for calorimeters
• current topics
  • understanding non-proportionality
  • Eu$^{2+}$ and Pr$^{3+}$ activated scintillators
  • scintillator pulse rise time studies
Acknowledgements

• Some of the materials for these slides were provided by
  • Dr. P. Schotanus, company Scionix, The Netherlands
  • Dr. E. Mattmann, company Saint Gobain crystals, France
  • Dr. A. Owens and F. Quarati, European Space Agency, Netherlands
  • Dr. J. Karp, Pennsylvanian State University, USA
References

- Radiation Detection and Measurements, G. Knoll, John Wiley&Sons, Inc
Thermal neutron scintillators

- Efficient thermal neutron detection
  - high capture cross section
    - suitable isotopes and isotope enrichment
  - absence of competing capture processes
- gamma ray background rejection
  - thin layers of low density
  - pulse height discrimination
  - pulse shape discrimination

Thermal neutron capture reactions

- \( n + ^6\text{Li} \rightarrow ^3\text{H} + \alpha + 4.79 \text{ MeV} \)
- \( n + ^{10}\text{B} \rightarrow ^{11}\text{B} \rightarrow ^7\text{Li} + \alpha + 2.78 \text{ MeV} \) (7%)
  \( ^7\text{Li}^* + \alpha + 2.30 \text{ MeV} \) (93%)

TU Delft
## inorganic thermal-neutron scintillators

<table>
<thead>
<tr>
<th>Scintill. host</th>
<th>Density $\rho$ g/cm$^3$</th>
<th>Abs. Length at 1.8 Å $\rho Z_{eff}^4$ (× 10$^6$) mm</th>
<th>$\lambda_{em}$ λ (nm)</th>
<th>Light yield photons per neutron MeV gamma</th>
<th>$\tau$ ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6$Li-glass</td>
<td>2.5</td>
<td>0.52</td>
<td>Ce</td>
<td>395</td>
<td>6.000  4.000</td>
</tr>
<tr>
<td>$^6$LiI</td>
<td>4.1</td>
<td>0.54</td>
<td>31 Eu</td>
<td>470</td>
<td>50,000 12,000</td>
</tr>
<tr>
<td>$^6$LiF/ZnS</td>
<td>2.6</td>
<td>0.8</td>
<td>1.2 Ag</td>
<td>450</td>
<td>160,000 75,000</td>
</tr>
<tr>
<td>$^6$Li$_6$Gd(BO$_3$)$_3$</td>
<td>3.5</td>
<td>0.35</td>
<td>25 Ce</td>
<td>385/415</td>
<td>40,000 20,000</td>
</tr>
</tbody>
</table>
Pulse shape discrimination due to core-valence luminescence in LiBaF$_3$:Ce$^{3+}$
LiBaF$_3$:Ce scintillator

C.M. Combes et al, NIM A416(1998)364

Spectra of radiation emitted by a Pu-Be source shielded with paraffine and 6 cm of lead

CVL does not respond to $^3$H (2.75 MeV) + $^4$He (2.05 MeV)

# 1 is without discrimination, # 2 with discrimination. The neutron peak at 750 keV gamma-equivalent energy is almost free from background
Thermal neutron detection with Cs$_2$LiYCl$_6$:0.1% Ce$^{3+}$

- Thermal neutron peak at 662 keV
- $\gamma$-equivalent energy (MeV)
  - $\alpha/\beta = 0.66$
  - R = 9%
  - 22000 ph/MeV
  - 70000 ph/neutron

- Pulse shape plus pulse height discrimination

- $\tau$ = 85 ns
- CVL $\tau$ = 4 ns

- Density $\rho = 3.3 \text{g/cm}^3$

- Intensity (arb. un.) vs. time (ns)
Thermal neutron scintillators

Selection of the scintillator based on thermal neutron detection efficiency

<table>
<thead>
<tr>
<th>σ (barn)</th>
<th>6Li - nat /%Σσ</th>
<th>6Li - 95enr /%Σσ</th>
<th>Absorption length 0.18 nm - 95enr (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs₂LiYBr₆</td>
<td>71/41</td>
<td>895/90</td>
<td>3.7</td>
</tr>
<tr>
<td>Rb₂LiYBr₆</td>
<td>71/62</td>
<td>895/95</td>
<td>3.5</td>
</tr>
<tr>
<td>Li₂NaYBr₆</td>
<td>142/77</td>
<td>1790/98</td>
<td>1.7</td>
</tr>
<tr>
<td>K₂LiYBr₆</td>
<td>71/60</td>
<td>895/95</td>
<td>3.5</td>
</tr>
<tr>
<td>Rb₂LiLaBr₆</td>
<td>71/58</td>
<td>895/95</td>
<td>3.5</td>
</tr>
<tr>
<td>Cs₂LiLuI₆</td>
<td>71/29</td>
<td>895/84</td>
<td>3.9</td>
</tr>
<tr>
<td>Rb₂LiYI₆</td>
<td>71/65</td>
<td>895/96</td>
<td>3.4</td>
</tr>
</tbody>
</table>
Thermal neutron scintillation light yield and peak resolution $\text{Rb}_2\text{LiYBr}_6$:Ce$^{3+}$

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Photons/neutron</th>
<th>$\alpha/\beta$ ratio</th>
<th>Peak resolution %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Rb}_2\text{LiYBr}_6$: 0.1% Ce$^{3+}$</td>
<td>59,000 ± 5,900</td>
<td>0.74</td>
<td>3.6</td>
</tr>
<tr>
<td>$\text{Rb}_2\text{LiYBr}_6$: 0.5% Ce$^{3+}$</td>
<td>83,000 ± 8,300</td>
<td>0.75</td>
<td>5.4</td>
</tr>
<tr>
<td>$\text{Rb}_2\text{LiYBr}_6$: 1% Ce$^{3+}$</td>
<td>49,000 ± 4,900</td>
<td>0.79</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>51,000 ± 5,100</td>
<td>0.82</td>
<td>4.2</td>
</tr>
<tr>
<td>$\text{Rb}_2\text{LiYBr}_6$: 5% Ce$^{3+}$</td>
<td>39,000 ± 3,900</td>
<td>0.74</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>42,000 ± 4,200</td>
<td>0.80</td>
<td>7.8</td>
</tr>
<tr>
<td>Scintill. host</td>
<td>Density $\rho$ g/cm$^3$</td>
<td>Abs. Length at 1.8 Å mm</td>
<td>$\lambda_{em}$ nm</td>
</tr>
<tr>
<td>---------------</td>
<td>--------------------------</td>
<td>--------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>$^6$Li Glass:Ce</td>
<td>2.5</td>
<td>0.52</td>
<td>395</td>
</tr>
<tr>
<td>Cs$_2$LiYBr$_6$:Ce$^{3+}$</td>
<td>4.1</td>
<td>3.7</td>
<td>389</td>
</tr>
<tr>
<td>Rb$_2$LiYBr$_6$:Ce$^{3+}$</td>
<td>4.8</td>
<td>3.5</td>
<td>385</td>
</tr>
<tr>
<td>Li$_2$NaYBr$_6$:Ce$^{3+}$</td>
<td>2.9</td>
<td>1.7</td>
<td>380</td>
</tr>
</tbody>
</table>

The table lists various scintillators with their density, absolute length at 1.8 Å, emission wavelength ($\lambda_{em}$), light yield in neutrons and MeV gamma, $\alpha/\beta$ ratio, and lifetime ($\tau$). The peak resolution is also provided.