Last trends in scintillators development; theory and practice

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119991, Moscow, Russia
Scintillation discovery

**Conventional scintillators**
- NaI:Tl, CsI, CsI:Na, CsI:Tl

**Ce\textsuperscript{3+} doped**
- Lu\textsubscript{3}Br\textsubscript{3}:Ce 2003
- LaBr\textsubscript{3}:Ce 2001
- LYSO:Ce 2001
- LuYAP:Ce 2001
- LaCl\textsubscript{3}:Ce 2000
- LuAP:Ce 1994
- LSO:Ce 1982

**Eu\textsuperscript{2+} doped**
- SrCsI\textsubscript{3}:Eu 2012
- BaBrI:Eu 2011
- Ba\textsubscript{2}CsI\textsubscript{5}:Eu 2009
- SrI\textsubscript{2}:Eu 2007

**Year**
- 1900
- 1920
- 1940
- 1960
- 1980
- 2000
- 2020
1949 – NaI(Tl) invention
1963 – Gamma-camera prototype
Large NaI(Tl) needs

1952 – 0,5" dia growth
1974 – 21" dia growth

Dr. Carl Swinehart
In Harshaw from 1932 to 1990

R&D supervisors !!!
Prof. R. Hofstadter (Stanford)
and Dr. D. Stockbarger (MIT)

Harshaw Chemical Company

NaI(Tl) way to Crystal Ball
Material: PWO  
Invention: 1991

PWO milestones:

1992 : Crystal-2000; PWO promotion  
1994 : Choice of PWO for CMS e-cal  
1994-1998 : extensive R&D on PWO  
1998-2000 : Preproduction of 6000 crystals  
2001 : Start of the production  
2008: E-cal complete

LHC - CERN
PbWO₄(PWO) cycle. From invention to LHC use

1992

1994-1999

Study and promotion

1997-2006

Technology R&D and production

2008

Start CMS at LHC

17 year cycle

What is next?
ISMA for International Collaborations

**High Energy and Nuclear Physics**

- CMS
- PANDA
- PiBeta (Switzerland)
- AGILE (Italy)
- BELLE (Japan)
- BaBar (USA)
- PiBeta (Switzerland)
- KEDR
- CALIFA (FAIR)
- OPERA
- NEMO

**Space Missions**

- GLAST (USA, Sweden…)
- AGILE (Italy)
Is it possible to improve scintillation efficiency of conventional scintillators?

**Optimal scintillator**

Effective = efficient + available + cheap

- **efficient** ~ 100,000 ph/MeV, 3% resolution (662 kev)
- **available** ~ size 400 mm
- **cheap** ~ 3 $/cc

**History (2008-2009) and start point:**

Two ways to obtain (develop) new efficient scintillator:

**A - search of new compounds (Successfully done!)**

(-) Deep scientific search !?
(-) Ability to grow large crystal ?
(-) Crystal cost ?

**B - modification of conventional scintillators**

(-) Need in modification idea ?!
(+) Existed technologies of industrial growth!
Logics and motivation

Scintillator applications

Imaging

- Medicine (PET)
  - Fast response
    - CV — luminescence
    - Ce$^{3+}$, Pr$^{3+}$ etc.

Spectroscopy

- Nuclear physics, Security
  - Medium or even slow response
    - Tl, Eu$^{2+}$ etc.
## Most efficient new scintillators

<table>
<thead>
<tr>
<th>Crystal</th>
<th>( \rho ), g/cm(^3)</th>
<th>Lum ( \lambda, ) nm</th>
<th>LY ph/Mev</th>
<th>R, ( % ) Cs(^{137})</th>
<th>Decay ( \tau, ) ns</th>
<th>Hygroscopy</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaI(_2) :Eu</td>
<td>3.96</td>
<td>467</td>
<td>110.000</td>
<td>5.2</td>
<td>1.000</td>
<td>strong</td>
<td>Cherepy, Moses, Derenzo, Bizarri, Bourret et al. 2007 - 2012</td>
</tr>
<tr>
<td>SrI(_2) :Eu</td>
<td>4.55</td>
<td>435</td>
<td>115.000</td>
<td>2.6</td>
<td>1.500</td>
<td>strong</td>
<td></td>
</tr>
<tr>
<td>Ba(_2)CsI(_5) :Eu</td>
<td>4.9</td>
<td>435</td>
<td>102.000</td>
<td>2.55</td>
<td>383; 1.500</td>
<td>medium</td>
<td>Zhuravleva et al. 2012</td>
</tr>
<tr>
<td>SrCsI(_3) :Eu</td>
<td>4.25</td>
<td>458</td>
<td>73.000</td>
<td>3.9</td>
<td>2.200</td>
<td>medium</td>
<td></td>
</tr>
<tr>
<td>BaBrI :Eu</td>
<td>5.2</td>
<td>413</td>
<td>97.000</td>
<td>3.4</td>
<td>500</td>
<td>low</td>
<td>Bizarri et al. 2011</td>
</tr>
<tr>
<td>NaI : Tl</td>
<td>3.67</td>
<td>415</td>
<td>44.000</td>
<td>5.6</td>
<td>230</td>
<td>strong</td>
<td></td>
</tr>
<tr>
<td>CsI : Tl</td>
<td>4.53</td>
<td>560</td>
<td>56,000</td>
<td>6.0</td>
<td>980</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>CsI : Na</td>
<td>4.20</td>
<td>460</td>
<td>46,000</td>
<td>6.4</td>
<td>600</td>
<td>low</td>
<td></td>
</tr>
</tbody>
</table>
Scintillator efficiency:

\[ N_{ph} = \beta S Q \]

\[ \beta = \frac{E\gamma}{E_{e-h}} \]

- \( E\gamma \) quantum energy
- \( E_{e-h} = \sim 2.4 E_g \)
- \( S \) energy transfer efficiency
- \( Q \) luminescence center efficiency

\( \beta \) – e-h creation efficiency is a key to the new material search and investigation

\( Q \) is \( \sim 1 \) for many typical activators, Ce, Eu etc

\( S \) is also \( \sim 1 \) for many hosts.

1-5% of uniform distributed activator minimizes the transfer length to 2-5 \( a \) (lattice parameters)

P.Dorenbos, SCINT, 2009
What was done last years?

- Maximal yield for alkali halides is far from the fundamental limit. *Some limits could be described*

- Why alkali-earth (AE) halides are more efficient? *The yield is close to fundamental limit*

- Can we obtain (grow) scintillators with the large size and high industrial efficiency? *Why not? What are the problems?*

- Natural “bottle neck” (self absorption). *Overpass ways*
Auger processes & X-ray fluorescence reabsorption

Thermalization of electrons

Creation of excitons, capture of electrons and holes by different traps, their self-trapping, etc.

Interaction of excitations

Emission

Thermalization of holes

Auger process threshold

Auger processes & X-ray fluorescence reabsorption
Auger processes & X-ray fluorescence reabsorption

Interaction and quenching of excitons and carriers

Emission

Defect creation

Migration of excitons and carriers

Trapping and releasing of carriers

Thermalization of excitons and excited states of centers

Thermalization of electrons and holes

Electron scattering and Auger cascade

Creation of excitons, capture of electrons and holes by different traps, their self-trapping, etc.

Auger process threshold

Auger processes & X-ray fluorescence reabsorption

E - E threshold
Electron scattering and Auger cascade

Thermalization of electrons and holes

Interaction and quenching of excitons and carriers

Recombination with creation of excitons and excited states of centers

Migration of excitons and carriers

Emission

Defect creation

Trapping and releasing of carriers

Are these processes independent? NO!
Recombination with creation of excitons and excited states of centers

Interaction and quenching of excitons and carriers

Emission

Migration of excitons and carriers

Defect creation

Trapping and releasing of carriers

Contemporary model incorporates the interconnection of all these processes.
Spatial scales for processes in scintillators

- Interaction (quenching) distance $R_{dd}$
- Activator to activator distances
- Onsager recombination radius
- Distances between elementary e-e scattering events – e-e mfp – function of hot electron energy
- Thermalization distances – function of secondary electron kinetic energy
- Overall track length – keV, MeV, GeV
- Geometry dimensions of media – macro-, meta- & nano-materials
- Activator to activator distances – concentration $1/3$
Outline

Spatial scales for processes in scintillators
Nanoparticles as scintillators
Cascade, thermalization and recombination
Different types of mobilities
Thermalization length for different types of crystals
Interconnection of cascade, thermalization and recombination stages in binary iodides
Why cascade is so effective in CsI?
Thermalization length and impurities
Concluding remarks
Trapping and releasing of carriers

Migration of excitons and carriers

Defect creation

Trapping and releasing of carriers

Emission

Recombination with creation of excitons and excited states of centers

Electron scattering and Auger cascade

Thermalization of electrons and holes

Interaction and quenching of excitons and carriers

Energy distribution

Spatial distribution
Spatial track structure for e-e scattering stage
(prior to thermalization)

‘Real’ track structure

Regions created by different virtual photons are overlapped
Spatial track structure for phonon scattering stage (after thermalization) for small thermalization radius

‘Real’ track structure

Regions created by different virtual photons are overlapped
Spatial track structure for e-h Onsager recombination stage for small thermalization radius

‘Real’ track structure

- Onsager radius: 10 nm

Regions created by different virtual photons are overlapped
3D diffusion-controlled recombination

Recombination probability

\[ P = \begin{cases} 
1, & r_{eh} < R_0 \\
R_0/r_{eh}, & r_{eh} > R_0 
\end{cases} \]

Black sphere

\[ P = 1 - \exp \left( -\frac{R_{Ons}}{r_{eh}} \right) \]

Coulomb

\[ \frac{e^2}{\varepsilon R_{Ons}} = k_B T \]

\( \varepsilon = 5.7 \quad T = 300K \quad R_{Ons} = 10 \text{ nm} \)

\( T = 77K \quad R_{Ons} = 38 \text{ nm} \)

\( T = 10K \quad R_{Ons} = 300 \text{ nm} \)

For thermalized excitations \( R_{Ons}/r_{eh} \ll 1 \)

- exciton yield after thermalization should be low

Simulated spatial distribution of e–h pairs for a 10 keV photon event in CsI, where electrons and holes are distinguished by size and color, as indicated in legend. NWEGRIM code.

Spatial track structure for e-h Onsager recombination stage for large thermalization radius

'Real' track structure

Onsager radius 10 nm
Example of structure of excited region after 30 keV electron passage
30 keV electron track, electron thermalization radius $r_{e,\text{th}} = 6$ nm, hole thermalization radius $r_{h,\text{th}} = 0.6$ nm
30 keV electron track, electron thermalization radius $r_{e,th} = 20$ nm, hole thermalization radius $r_{h,th} = 5$ nm
30 keV electron track,
\( r_{e,\text{th}} = 6 \text{ nm} \),
\( r_{h,\text{th}} = 0.6 \text{ nm} \) (\textbf{red}=e, \textbf{blue}=h)
30 keV electron track, $r_{e,th}=20$ nm, $r_{h,th}=5$ nm (red=$e$, blue=$h$)
Outline

Spatial scales for processes in scintillators
Nanoparticles as scintillators
Cascade, thermalization and recombination
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Thermalization length for different types of crystals
Interconnection of cascade, thermalization and recombination stages in binary iodides
Why cascade is so effective in CsI?
Thermalization length and impurities
Concluding remarks
Electron-hole separation and recombination

- Thermalization
- Diffusion of thermalized carriers
- Geminate recombination
- Bimolecular recombination and escape
Electron-hole separation and recombination

- Thermalization
- Diffusion of thermalized carriers
- Geminate recombination
- Bimolecular recombination and escape
- Stochastic $e-h$ recombination & escape
- Direct exciton creation
- Geminate $e-h$ recombination

Thermalization length / Onsager radius
How we can manage thermalization length?

What we have to do to improve the yield?

The goal is to concentrate e-h pairs at the distance less than the Onsager radius, to minimize the volume of stochastic recombination and escape losses.

Two ways for e-h separation management

Doped/activated crystals (rare solutions)

Mixed crystals (hard solutions)

Z. Wang, Y. Xie, B. D. Cannon… 2011
Coupled processes of thermalization and spatial diffusion

Mean square of the thermalization distance
\[ < r^2 >_{E_e \to E_e^{\text{kin}}} = 6 \int_{E_e^{\text{kin}}}^{E_e} \frac{D^R(E')}{S(E')} dE' \]

Spatial distribution function
\[ f(r, l_e(E_e)) = \frac{3\sqrt{6}}{\sqrt{\pi}} \frac{r^2}{l_e^3(E_e)} \exp \left( -\frac{3r^2}{2l_e^2(E_e)} \right) \]

where thermalization length is
\[ l_e(E_e) = \sqrt{< r^2 >_{E_e \to k_B T}} \]

Thermalization length for one LO phonon branch
\[ l_{e,LO}^2(E_e) = \frac{8}{3} a_B^2 \left( \frac{\bar{\varepsilon}}{m_e^*/m_0} \right)^2 \tanh \left( \frac{\hbar \Omega_{LO}}{2k_B T} \right) \frac{E_e^0}{\hbar \Omega_{LO}} \frac{E'}{\hbar \Omega_{LO}}^2 \frac{1}{\ln(4E'/\hbar \Omega_{LO})} \frac{dE'}{\hbar \Omega_{LO}} \]

\[ = \frac{1}{24} a_B^2 \left( \frac{\bar{\varepsilon}}{m_e^*/m_0} \right)^2 \tanh \left( \frac{\hbar \Omega_{LO}}{2k_B T} \right) \text{Ei} \left( 3 \ln \left( \frac{4E_e^0}{\hbar \Omega_{LO}} \right) \right) \]

We have to choose/engineer materials with
- higher effective masses in the whole relaxation region \( E_{\text{kin}} < E_g \)
- higher LO phonon energies
Spatial distribution of electrons, holes and excitons due to mobility in e-e passive energy domain

Two types of carrier mobilities: thermalization length (mobility of hot electrons and holes) and mobility of thermalized excitations (electrons, holes & excitons).

*High-energy part of ionization track* – individual electron-hole pairs and small non-overlapping clusters of excitations. **Negative role of mobility**: the higher thermalization length (in comparison with Onsager radius), the lower the recombination yield.

*Low-energy part of ionization track* – overlapping clusters of excitations. Mean distance between interacting excitations increases with increase of the mobility of excitons. **Positive role of mobility**: the higher the mobility, the lower the quenching of excitation due to high EE density.

**“Ideal” scintillator**: Low hot mobility (high yield of excitons) and high thermalized mobility (low interaction).
Binary alkali halides:

Can the yield achieve theoretical limit?

Can we improve conventional alkali halide scintillators?
Fundamental limits to Light Yield of NaI and CsI based scintillators (LY vs. $E_g$)

Experimental data are far from theoretic limit for NaI and CsI based crystals

Pure NaI and CsI possess extremely high photon yield at LNT

[V.Sciver, 1958; Persyk, 1980; Moszynski et al, 2010]
Resume:
* It is possible to separate different types of emission
* STE and defect trapped exciton emissions are dominated
* Self trapping creates the best conditions for maximal yield
* Other relaxation mechanisms lead to an extra efficiency losses
Non-proportionality analysis for alkali halides

The high-energy decrease of the scintillator efficiency shows that significant fraction of individual electron-hole pairs are thermalized at distances larger than Onsager radius. We can increase Onsager radius – by decreasing the temperature. Pure CsI and NaI have yield ~ 100,000 ph/MeV at 77K! \(R_{\text{ons,77K}}=4R_{\text{ons,300K}}\)

We can decrease thermalization distances - by choosing of complex halides.

What is the physics of the thermalization distances decrease in this case?

Electron response of some scintillators
[S. A. Payne, W. W. Moses et al., IEEE TNS, 2011]
Starting states for thermalization ($E_{\text{kin}} < E_g$)

Thermalization for parabolic band and one LO phonon starting from energy $E_0$

\[
l_{e,LO}(E_{e0}) = \frac{1}{24} d_B^2 \left( \frac{\bar{E}}{m_e/m_0} \right)^2 \tanh\left( \frac{\hbar \Omega_{LO}}{2k_B T} \right) \text{Ei}\left( \frac{3 \ln \left( \frac{4E_{e0}}{\hbar \Omega_{LO}} \right)}{2} \right),
\]

\[
f(r, l_e(E_{e0})) = \frac{3\sqrt{6} r^2}{\sqrt{\pi} L_e^2(E_{e0})} \exp\left( - \frac{3r^2}{2L_e^2(E_{e0})} \right)
\]

Spatial distribution of thermalized electrons (binary crystals)

<table>
<thead>
<tr>
<th></th>
<th>$R_{Ons}$, 300K</th>
<th>Yield, 300K</th>
<th>Yield, 77K</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsI</td>
<td>9.87 nm</td>
<td>0.24</td>
<td>0.44</td>
</tr>
<tr>
<td>NaI</td>
<td>9.05 nm</td>
<td>0.34</td>
<td>0.58</td>
</tr>
</tbody>
</table>
Can we use co-doping to collect more excitations?

Eu, Ti – co-doping of NaI increases light yield comparing to conventional NaI:Tl
<table>
<thead>
<tr>
<th>Crystal</th>
<th>Ti, m%</th>
<th>Eu, m%</th>
<th>Lum, nm</th>
<th>Decay, ns</th>
<th>LY, %</th>
<th>R, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaI-Tl</td>
<td>$1 \cdot 10^{-1}$</td>
<td>415</td>
<td>230</td>
<td>100</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>NaI-Tl, Eu</td>
<td>$1 \cdot 10^{-1}$</td>
<td>$1 \cdot 10^{-3}$</td>
<td>445</td>
<td>230 (26%)</td>
<td>110</td>
<td>6.2</td>
</tr>
<tr>
<td>NaI-Eu</td>
<td>$1 \cdot 10^{-1}$</td>
<td>445</td>
<td>1000</td>
<td>60</td>
<td>9.5</td>
<td></td>
</tr>
</tbody>
</table>

- Introduce of hundred times lower Eu-concentration ($10^{-3}\%$) than Ti ($0.1\%$) leads to Ti emission suppression and higher light output.
- Thus, Eu co-doping allows to get better scintillation performance of NaI:Tl.
- It costs some losses at decay and claim for larger integration time.
Binary alkali halides - the yield could not reach fundamental limit!

✓ The maximal CsI or NaI scintillation yield corresponds to STE relaxation at LNT

✓ Temperature rise leads to the STE luminescence quenching and DTE emission that lower due to transfer and stabilization losses. Eu$^{2+}$ co-doping allows slightly increase the NaI(Tl) yield only

✓ Thermalization length is much higher than Onsager radius in alkali halides – therefore geminate recombination yield is much less then unity.

✓ We can decrease thermalization distances – by choosing of complex halides
What materials are characterized by lower thermalization length? Why Alkali Earth Halides?

How thermalization length depend on material parameters?

\[ l_{e,LO}^2(E_{e0}) = \frac{1}{24} a_B^2 \left( \frac{\varepsilon}{m_e^* / m_0} \right)^2 \tanh \left( \frac{\hbar \Omega_{LO}}{2k_BT} \right) \text{Ei} \left( 3 \ln \left( \frac{4E_{e0}}{\hbar \Omega_{LO}} \right) \right), \]

We should choose materials with

- **higher effective masses** in the whole relaxation region \( E_{\text{kin}} < E_g \) and

- higher LO phonon energies

Why AE halides? - Lower thermalization length in complex halides result in higher yield of geminate recombination!

Complex halides with many atoms in elementary cell (e.g. Srl\(_2\) with 24 atoms in elementary cell)
Comparison of CsI and SrI$_2$ electronic structures

- SrI$_2$ thermalization length is much shorter than for CsI (and anisotropic)
- Mean velocities of non-relaxed electrons and holes for SrI$_2$ are much less than for CsI

$v=5.4 \times 10^5$ m/s

$\Gamma$-X=6.95 nm$^{-1}$

$\Gamma$-X=3.92 nm$^{-1}$

For all complex halides we can obtain high yield due to high yield of geminate recombination and small bimolecular effects in non-proportionality curves.

Lower thermalization length (in comparison with alkali halides) is connected with:
- flat bands in whole energy thermalization region ($E_{\text{kin}} < E_g$)
- much more complicated LO phonon structure (and probably strongly anisotropic mobility due to layer structure)
Renaissance of Eu-doped scintillators (history and reality)

New demands have led to discovery of several new Eu-doped scintillators

<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td><strong>LiCl :Eu</strong></td>
<td><strong>Cal$_2$ :Eu</strong></td>
</tr>
<tr>
<td>Lehmann, 1975</td>
<td>LLNL, LBNL, USA</td>
</tr>
<tr>
<td><strong>Li$I$ :Eu</strong></td>
<td><strong>SrI$_2$ :Eu</strong></td>
</tr>
<tr>
<td>Murray, 1958</td>
<td>Cherepy, Moses et al.</td>
</tr>
<tr>
<td><strong>Cal$_2$ :Eu</strong></td>
<td>2007 - 2009</td>
</tr>
<tr>
<td>Hofstadter, 1963</td>
<td><strong>Ba$_2$Csl$_5$ :Eu</strong></td>
</tr>
<tr>
<td>Lyskovitch, 1970</td>
<td>LBNL, USA</td>
</tr>
<tr>
<td><strong>CaF$_2$ :Eu</strong></td>
<td><strong>BaBrI :Eu</strong></td>
</tr>
<tr>
<td>Butement, 1948</td>
<td>Bourret, Derenzo et al.</td>
</tr>
<tr>
<td><strong>SrCl$_2$ :Eu</strong></td>
<td>2010</td>
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<tr>
<td>Lehmann, 1975</td>
<td><strong>BaFl :Eu</strong></td>
</tr>
<tr>
<td><strong>SrBr$_2$ :Eu</strong></td>
<td><strong>SrCsl$_3$ :Eu</strong></td>
</tr>
<tr>
<td><strong>SrI$_2$ :Eu</strong></td>
<td>SMRC, Tennessee, USA,</td>
</tr>
<tr>
<td>scintillator</td>
<td>Zhuravleva, Melcher et al. 2010</td>
</tr>
</tbody>
</table>
Pulse height spectra of record scintillators under γ^{137}Cs excitation

BaBrI:Eu

CsBa_{2}I_{5}:Eu

BaBrCl:Eu

LBNL, USA
Bourret, Derenzo, Bizarri et al. 2009-2012
## AE scintillator performance progress (2007→2012)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>2007 - 2009</th>
<th>2011 - 2012</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LY ph/Mev</td>
<td>R, % Cs\textsuperscript{137}</td>
</tr>
<tr>
<td>SrI\textsubscript{2}:Eu</td>
<td>115.000</td>
<td>2.6</td>
</tr>
<tr>
<td>Ba\textsubscript{2}CsI\textsubscript{5}:Eu</td>
<td>97.000</td>
<td>3.8</td>
</tr>
<tr>
<td>SrCsI\textsubscript{3}:Eu</td>
<td>65.000</td>
<td>5.2</td>
</tr>
<tr>
<td>BaBrI:Eu</td>
<td>81.000</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Many AE halides possess with efficiency about fundamental limit.

Selection of one (best) scintillator has to base on the technology advantages.
Modification of phonon spectrum (additional phonon branches)

Mixed – $A_x B_{1-x} C$ crystal model

Density of LO states

- $x=0$
- $x=0.25$
- $x=0.5$
- $x=0.75$
- $x=1$

Thermalization length decrease

Probability of geminate recombination

Recombination probability increase

Solid solution of binary crystals $A_x B_{1-x} C$
$E_{LO}(AC)=50$ meV
$E_{LO}(BC)=10$ meV

Electron kinetic energy
0.5 eV
1 eV
3 eV
5 eV
Modification of electron spectrum – increasing of elastic scattering

Solid solution of binary crystals

\[ A_x B_{1-x} C \]

\[ E_{LO}(AC)=50 \text{ meV} \]
\[ E_{LO}(BC)=10 \text{ meV} \]

Mean thermalization length, nm

Electron kinetic energy

0.5 eV
1 eV
3 eV
5 eV

Mean distance \(<r^2>^{1/2}\) (nm)

Electron energy (eV)

\[ x=0 \]
\[ x=0.5 \]
\[ x=0.95 \]
\[ x=1 \]

\[ k_B T \]
Mixed fluorides: $\text{Ce}_x\text{La}_{1-x}\text{F}_3$

Pulse shape and decay kinetics of $\text{Ce}_x\text{La}_{1-x}\text{F}_3$

X-ray excitation (10 keV).

Left – original linear scale data; right – intensity vs cation mixture rate.

A.N. Belsky, A.V. Gektin et al., Proceedings of SCINT'95, Delft, 1995
Mixed halides... 20 years late

Emission spectra under UV excitation

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**SCINTILLATOR COMPOSITIONS, AND RELATED PROCESSES AND ARTICLES OF MANUFACTURE**

Srivastava et al.  
Date of Patent: Aug. 1, 2006

**TABLE 1**

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>COMPOSITION</th>
<th>ACTIVATOR</th>
<th>LIGHT OUTPUT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A**</td>
<td>LaBr₃</td>
<td>—</td>
<td>100</td>
</tr>
<tr>
<td>B**</td>
<td>LaCl₃</td>
<td>—</td>
<td>68</td>
</tr>
<tr>
<td>C</td>
<td>La(Cl₀.₆₆Br₀.₃₄)₃</td>
<td>CeCl₃</td>
<td>132</td>
</tr>
<tr>
<td>D</td>
<td>La(Cl₀.₃₄Br₀.₆₆)₃</td>
<td>CeBr₃</td>
<td>126</td>
</tr>
<tr>
<td>E</td>
<td>La(Cl₀.₆₆Br₀.₃₄)₃</td>
<td>CeBr₃</td>
<td>120</td>
</tr>
<tr>
<td>F</td>
<td>La(Cl₀.₃₄Br₀.₆₆)₃</td>
<td>CeCl₃</td>
<td>138</td>
</tr>
</tbody>
</table>

*Relative percent for samples B–F, as compared to sample A. **Comparative samples.
e-h separation and/or conduction band modification?

Band structure change with Ga doping.

Ga doping (shift to mixed crystals)
* Decrease the CB bottom level
  • Decrease of shallow traps influence
  • ....

M.Nikl ...

* There are some alternative mechanisms that influence to light yield with similar or even higher rate

** Crystal performance, initial purity and activator concentration are crucial for the experimental study of phenomena

*** Decay time measurement could be more efficient for the model verification than yield test

**** We need in more detailed theoretical estimations for doped and mixed crystals
CONCLUSIONS

CsI-CsBr

Ce\textsubscript{x}La\textsubscript{1-x}F\textsubscript{3}

LaCl\textsubscript{3}-LaBr\textsubscript{3}

(Lu, Y)Al\textsubscript{2}O\textsubscript{3}: Ce

LGSO:Ce

Zn\textsubscript{x}Mg\textsubscript{1-x}WO\textsubscript{4}

Ca\textsubscript{1-x}Sr\textsubscript{x}S

YAGG:Ce

Gd\textsubscript{2}(Al\textsubscript{x}Ga\textsubscript{1-x})\textsubscript{5}O\textsubscript{12}:Ce
Modification of kinetics in scintillators

Scintillator kinetics

\[ \text{Luminescence quenching due to interaction in the regions with high concentration of excitations} \]

\[ \text{Essentially non-exponential decay kinetics for pure NaI} \]

\[ I \sim \frac{A}{(1 + t/t_0)^2} + B \]

\( \tau = 93 \text{ ns} \)

CRYSTAL GROWTH,

RAW MATERIAL,

TARGET PRICE

FOR ALKALI-EARTH HALIDES
Two ways to increase industrial output

1. Increase of crystal / crucible diameter

   - Increased power input
   - Melt turbulences

   Czochralski

2. Lengthening of crystal / melt height

   - Increased interaction with ampoule
   - Increasing melt convection

   VGF

P. Rudolf, IWCGT 2008
Continuous growth procedure
NaI(Tl) crystal continuous growth
From Principles to Practice

Nal(Tl)
Industrial growth

*Hygroscopicity is not a problem!*

Si – large size crystal growth

*Si - industry is an example of efficient and cost reasonable crystals production*
Crystal purity – crystal quality

Growth “chemistry”

\[
\begin{align*}
\text{MeO} + 2\text{HI} & \iff \text{MeI}_2 + \text{H}_2\text{O} \\
2\text{MeO} + \text{C}_2\text{I}_4 & \iff 2\text{MeI}_2 + 2\text{CO} \\
2\text{MeO} + \text{Cl}_4 & \iff 2\text{MeI}_2 + \text{CO}_2 \\
2\text{MeO} + 2\text{I}_2 & \iff 2\text{MeI}_2 + \text{O}_2 \\
\text{MeO} + \text{Cl}_4 & \iff \text{MeI}_2 + \text{CO} + \text{I}_2 \\
\text{MeO} + \text{I}_2 + \text{CO} & \iff \text{MeI}_2 + \text{CO}_2
\end{align*}
\]

Computer control
Rotary pump
Diffusion pump
10^{-10}
45
Gas cleaner (NaOH)
Graphite heater
Chamber
CZ furnace with resistive heater

Pulling rate: 1.0 mm/h
Rotation rate: 15 rpm
Orientation: a-axis
Composition: stoichiometric + 1 mol% AlF\textsubscript{3}, LiF (Colquiriites)

IR spectra of SrI\textsubscript{2}:Eu

Peaks demonstrate oxygen impurities inside
## Current prices for halides powder

<table>
<thead>
<tr>
<th>Product</th>
<th>Producer</th>
<th>Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrI₂</td>
<td>Russia</td>
<td>4N $1200/kg</td>
</tr>
<tr>
<td></td>
<td>USA</td>
<td>4N $3500/kg</td>
</tr>
<tr>
<td></td>
<td>India</td>
<td>2N $1300/kg</td>
</tr>
<tr>
<td>EuI₂ *</td>
<td>Russia</td>
<td>4N ~ $8000/kg</td>
</tr>
<tr>
<td></td>
<td>USA</td>
<td>4N ~ $20000/kg</td>
</tr>
<tr>
<td>BaBr₂</td>
<td>Russia</td>
<td>4N ~ $1000/kg</td>
</tr>
<tr>
<td>BaI₂</td>
<td>Russia</td>
<td>4N ~ $1000/kg</td>
</tr>
<tr>
<td>CsI</td>
<td>USA</td>
<td>5N $150/kg</td>
</tr>
<tr>
<td></td>
<td>Germany</td>
<td>5N $160/kg</td>
</tr>
<tr>
<td></td>
<td>Ukraine</td>
<td>5N $150/kg</td>
</tr>
</tbody>
</table>

*Eu₂O₃ price $3500-4500/kg (base for EuI₂)

### Target price estimation for hydrated AE halides

<table>
<thead>
<tr>
<th>Product name</th>
<th>Price per anhydrous</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrI₂ hydrate</td>
<td>$220-270/kilo</td>
</tr>
<tr>
<td>BaBr₂ hydrate</td>
<td>$150-200/kilo</td>
</tr>
<tr>
<td>BaI₂ hydrate</td>
<td>$150-200/kilo</td>
</tr>
</tbody>
</table>
Srl₂:Eu performance and cost vs. raw material purity

Srl₂. Raw material cost depending on purity

Srl₂:Eu. Energy resolution vs raw material purity
Crystal cost structure (Si)
- 68% - raw material
- 10% - crucible
- 8% - system cost
- 4% - labor cost
- 4% - power
- 6% - other

Oxides
- 20% - crucible
- 17% - power

Cost structure for single crystal growth

2010 prices
• Natural “bottle neck” (self-absorption) and *overpass ways*
Self-absorption due to small Stokes shift is the key problem for large bulk Eu doped scintillator use.

This is typical for all Eu doped crystals.!!!

*Self-absorption lead to the low transparency and scintillator efficiency loss*

J. Glodo et al. 2010

## Stokes shifts in Eu-doped scintillators

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Stokes shift, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkali halides</strong></td>
<td></td>
</tr>
<tr>
<td>NaI (Tl)</td>
<td>1.35</td>
</tr>
<tr>
<td>NaI (Eu)</td>
<td>0.8</td>
</tr>
<tr>
<td>CsI (Tl)</td>
<td>1.93</td>
</tr>
<tr>
<td>CsI (Na)</td>
<td>2.07</td>
</tr>
<tr>
<td>CsI (In)</td>
<td>1.83</td>
</tr>
<tr>
<td>CsI (Eu)</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Alkali-earth halides</strong></td>
<td></td>
</tr>
<tr>
<td>Srl₂ (Eu)</td>
<td>0.15</td>
</tr>
<tr>
<td>CaI₂ (Eu)</td>
<td>0.30</td>
</tr>
<tr>
<td>Ba₂CsI₅ (Eu)</td>
<td>0.15</td>
</tr>
<tr>
<td>CsSrI₃ (Eu)</td>
<td>0.55</td>
</tr>
<tr>
<td>BaBrI (Eu)</td>
<td>0.40</td>
</tr>
</tbody>
</table>

AE scintillator have a small Stokes shift and low transparency.

Light collection for high (0.01 cm⁻¹) and low (0.5 cm⁻¹) transparent crystals

V.A. Tarasov, ISMA, 2011

**Resume:**

Bulk Eu-doped scintillator could not be efficient scintillators.
Combined (phoswich) detectors as a way to increase scintillator efficiency

Gamma registration efficiency at 0.06 – 2.65 MeV for 0.5 cm thick SrI$_2$(Eu) combined with 10 cm NaI(Tl)

Signal separation due to decay time difference

<table>
<thead>
<tr>
<th>Scintillator</th>
<th>Decay Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrI$_2$:Eu</td>
<td>1200ns</td>
</tr>
<tr>
<td>NaI : Tl</td>
<td>230ns</td>
</tr>
<tr>
<td>BaBrI : Eu</td>
<td>500ns</td>
</tr>
<tr>
<td>CsBa$_2$I$_5$:Eu</td>
<td>383; 1200ns</td>
</tr>
<tr>
<td>CsI : Tl</td>
<td>980ns</td>
</tr>
</tbody>
</table>

Light collection coefficient for SrI$_2$:Eu and SrI$_2$(Eu)+NaI(Tl) phoswich detectors 4 cm thickness

V.A. Tarasov, ISMA, 2012
Conclusions

 ✓ The last years scintillators developments significantly upscale our vision of the perfect scintillator.

 ✓ Practical needs rise up theoretical studies and view to the fundamental process in radiation absorptions and primary stages of excited states relaxation (evolution).

 ✓ Theoretical simulations allow to select the process “skeleton” to make new material search more predictable.

 ✓ Next years forecast –
   - community has to select two-three best candiated for the technology development
   - we need in criteria for the best scintillators selection
THANK YOU FOR ATTENTION!