Scintillation efficiency improvement by mixed crystal use

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Motivation and outlines

• Can we use advantages of the last years theoretical studies for some practical use? *We mean the model of thermalisation stage responsibility for the later survival of electron excitation*

• What is following from the general model? How to apply this knowledge to doped crystals?

• Can we manage the thermalization distance by :
  – doping (rare solutions)
  – move to the mixed crystals (heavy solutions)

• Experimental data... old data, last results, perspectives

• Alternative mechanisms
Maximal scintillator light yield

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
Primary stages of scintillation (track formation and energy relaxation)

Main contributors to the track theory developments:

• R.T. Williams, .... see - SCINT – O2.9, O2.19, O6.6
• A.N. Vasil’ev... see – SCINT – O5.6, O5.9
• S. Kerisit, Z. Wang, F. Gao...
• A. Canning ... see – SCINT – O7.5
• V. Nagirnyi, M. Kirm... See – SCINT - O2.2
• W. Setyawan... et al
Scintillation process; from the absorption to photon emission

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

- Ionization by fast electrons, e-e inelastic scattering, Auger cascade
- Thermalization, formation of track structure
- Density-dependent STH+e→STE reaction \( W_{eh-ex} \)
- Density-dependent STE-STE quenching; Thermal STE quenching; STE quenching on defects \( W_{ex}^q \)
- Capture by defects \( W_h^d \)
- Capture by defects

\[ \eta = \frac{E}{E_{eh}} \left[ f_{ex} + (1 - f_{ex}) \frac{W_{eh-ex}}{W_h^d + W_{eh-ex}} \right] \frac{W_{ex}^r}{W_{ex}^r + W_{ex}^q} \]

A.Vasil’ev, A.Gektin - O5.6 (yesterday)
3D diffusion-controlled recombination

Recombination probability

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

Coulomb

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

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

\[ \varepsilon = 5.7 \]

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

– 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.

Spatial distribution of thermalized electrons (binary crystals)

See Vasil’ev, O5.6

<table>
<thead>
<tr>
<th></th>
<th>ROns, 300K</th>
<th>Yield, 300K</th>
<th>Yield, 77K</th>
</tr>
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<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>

Analytical estimation

Yield vs $E_{\text{kin}}$, 300K

Recombination yield

Electron kinetic energy, eV

Spatial distribution, nm

ROns, 10K

ROns, 77K

ROns, 300K

See Vasil’ev, O5.6
Electron-hole separation and recombination

- Geminate recombination
- Bimolecular recombination and escape

Thermalization
Diffusion of thermalized carriers

Successful
Electron-hole separation and recombination

Geminate recombination

Thermalization

Diffusion of thermalized carriers

Bimolecular recombination and escape

stochastic e-h recombination & escape

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 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

See also S.Gridin…O5.9
Coupled processes of thermalization and spatial diffusion

Mean square of the thermalization distance

\[ <r^2>_{E_{e_0} \rightarrow E_{e_0}^{\text{kin}}} = 6 \int_{E_{e_0}^{\text{kin}}}^{E_{e_0}} \frac{D^R(E')}{S(E')} dE' \]

Spatial distribution function

\[ f(r, l_e(E_{e_0})) = \frac{3\sqrt{6} r^2}{\pi l_e^3(E_{e_0})} \exp\left(-\frac{3r^2}{2l_e^2(E_{e_0})}\right) \]

where thermalization length is

\[ l_e(E_{e_0}) = \sqrt{<r^2>_{E_{e_0} \rightarrow k_BT}} \]

Thermalization length for one LO phonon branch

\[
l_{e,LO}^2(E_{e_0}) = \frac{8}{3} a_B^2 \left( \frac{\varepsilon}{m_e^*/m_0} \right)^2 \tan\left( \frac{\hbar \Omega_{LO}}{2k_BT} \right) \int_{h\Omega_{2,LO}}^{E_{e_0}} \left( \frac{E'}{h\Omega_{LO}} \right)^2 \frac{1}{\ln(4E'/h\Omega_{LO})} h\Omega_{LO} dE'
\]

\[
= \frac{1}{24} a_B^2 \left( \frac{\varepsilon}{m_e^*/m_0} \right)^2 \tan\left( \frac{\hbar \Omega_{LO}}{2k_BT} \right) \text{Ei}\left(3 \ln\left( \frac{4E_{e_0}}{\hbar \Omega_{LO}} \right)\right),
\]

We have to choose/engineer materials with

- higher effective masses in the whole relaxation region \( E_{\text{kin}} < E_g \)
- higher LO phonon energies
Possible mechanisms of reduction of electron-hole separation in solid solutions

- **Modification of hot stage of relaxation**
  - Modification of phonon spectrum (additional phonon branches)
  - Modification of electron spectrum – increasing of elastic scattering (Bragg scattering in case of regular crystal)

- **Modification of diffusion of thermalized carriers**
  - Non-uniformity of solution (in particular, clusterization) and scattering
  - Anderson localization of carriers in disordered systems
Modification of phonon spectrum (additional phonon branches)

Density of LO states

Mixed – $A_xB_{1-x}C$ crystal model

Mean thermalization length vs $X$ concentration

Probability of geminate recombination

Thermalization length decrease

Recombination probability increase
Modification of electron spectrum – increasing of elastic scattering (Bragg scattering in case of regular crystal)

![Graph showing electron kinetic energy and mean thermalization length](image)

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

- Mean thermalization length, nm
- Electron kinetic energy (eV): 0.5, 1, 3, 5
- Mean distance $<r^2>^{1/2}$ (nm)
- $k_B T$

Electron energy (eV) vs. Mean distance $<r^2>^{1/2}$ (nm) for different compositions $x$: 0, 0.5, 0.95, 1.
Scintillator kinetics

Luminescence quenching due to interaction in the regions with high concentration of excitations

Long component (migration)

Rising part (migration)

Essentially non-exponential decay kinetics for pure NaI

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

From the theory to experiment

• The database... Old and new experimental data

• The yield and decay kinetics analysis...

• Selection of proper experimental conditions (the same growth and components, activator content structure etc)

• No “masked phenomena”
Mixed halides. CsI-CsBr

First note – 1987

(Kubota… Gektin, Shiran)

Fast CsI scintillator...

Fig.1. a) Radioluminescence spectra of mixed CsI–CsBr1–x crystals:
   (1) x=0.01(1), x = 0.08 (2), x = 0.45 (3),
   x=0.8 (4), x = 1 (5).
   (b) Maximum position of UV emission band on the content of mixed components.

A. Gektin, N. Shiran, V. Shlyahturov and A. Belsky, Proceedings of SCINT’95, Delft, 1995

Fig.2. Concentration dependence of intensity (a) and light output (b) of CsI-CsBr crystals.

Mixed halides. CsI-CsBr

X-ray emission spectra and decay kinetics of CsI$_{1-x}$Br$_x$ solid solutions

A.N. Belsky, A.V. Gektin et al.,
Proceedings of SCINT’95, Delft, 1995
Interaction of excitations in the regions with high excitation concentration

CsI-CsBr (data reconstruction)

* Pulse intensity increase with simultaneous decay time shortening

• Similar behavior for CsI:CsCl

• Problem is the limited solubility

Dipole-dipole transfer:

\[
I_{lum}(t, n_0(r)) = \frac{n_0(r)}{\tau_r} \frac{\exp\left(-\frac{t}{\tau_r}\right)}{1 + \frac{2\pi^2}{3} n_0(r) R_{d-d}^3 \text{erf}\left(\sqrt{\frac{t}{\tau_r}}\right)}
\]

* Pulse intensity increase with simultaneous decay time shortening
• Similar behavior for CsI:CsCl

\[R_{d-d} = 2.1\ \text{nm for CdWO}_4\]

\[R_{d-d} = 2.9\ \text{nm for CsI}\]

M. Kirm et al, PRB 79, 233103 (2009)

R.T. Williams et al, PSS(b) 248, 426 (2011)
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

TABLE 1

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>COMPOSITION</th>
<th>ACTIVATOR</th>
<th>LIGHT OUTPUT*</th>
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<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>LaCl₀.₆₆Br₀.₃₄</td>
<td>CeCl₃</td>
<td>132</td>
</tr>
<tr>
<td>D</td>
<td>LaCl₀.₃₄Br₀.₆₆</td>
<td>CeBr₃</td>
<td>126</td>
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<tr>
<td>E</td>
<td>LaCl₀.₆₆Br₀.₃₄</td>
<td>CeBr₃</td>
<td>120</td>
</tr>
<tr>
<td>F</td>
<td>LaCl₀.₃₄Br₀.₆₆</td>
<td>CeCl₃</td>
<td>138</td>
</tr>
</tbody>
</table>

*Relative percent for samples B–F, as compared to sample A.
**Comparative samples.
Sulphides: $\text{Ca}_{1-x}\text{Sr}_x\text{S}$

Ce$^{3+}$ luminescence spectra for the solid solution (mixed crystals) of $\text{Ca}_{1-x}\text{Sr}_x\text{S}$ at X-ray excitation (30 kW, 10 mA)

Figure 2. Luminescence spectra of Ce$^{3+}$ in the concentration range of solid solutions $\text{Ca}_{1-x}\text{Sr}_x\text{S}$ (x-ray tube excitation: $T = 300$ K).

Oxides: LuYAP

(2000-2001)

Amplitude distribution of scintillation pulses under Cs X-ray excitation:

(a) LuAP:Ce,
(b) LuYAP(70%Lu):Ce,
(c) YAP:Ce.
(d) Light yield measured in Ce-doped Lu Y AlO crystals of various composition.

Lu$_{0.5}$Y$_{0.5}$AlO$_3$-Ce

Excitation and luminescence spectra of (Lu,Y)AlO$_3$-Ce

Excitation of Lu$_{0.5}$Y$_{0.5}$AlO$_3$-Ce

Intensities, a.u.

Energy, eV

Intensity, a.u.

Energy, eV

Intensity, a.u.

Yang et al., Proceedings of SCINT ’99, Moscow, 1999
Gamma excitation amplitude spectra of (Lu,Y)AlO₃-Ce.

(Single photon counting)
Mixed Borates – (Lu-Sc)BO$_3$:Ce

Y. Wu et al. / Journ Alloys Comp 509 (2011) 366–371
Luminescence spectra of $\text{Lu}_{0.75}\text{Y}_{0.25}\text{BO}_3:\text{Eu}^{3+}$

$E_{\text{ex}} = 5.4 \text{ eV (1)}$ and $E_{\text{ex}} = 5.9 \text{ eV (2)}$. 

[D. Spassky, ISMART 2012, Dubna, 2012]
Excitation spectra of $\text{Lu}_x\text{Y}_{1-x}\text{BO}_3:\text{Eu}^{3+}$

with

- $x = 0$ (curve 1),
- $x = 0.25$ (2),
- $x = 0.5$ (3),
- $x = 0.75$ (4),
- $x = 1$ (5),

$\lambda_{\text{em}} = 590$ nm, $T = 300$ K.
Oxides (intrinsic luminescence) - $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$

**Excitation and luminescence spectra**

![Excitation and luminescence spectra graph]

**Graph 1:**
- LHT$_{\text{in}}$ = 500 nm, corrected, normalized on the intensity of the first peak.
- Samples: MgWO$_4$, Mg$_{0.2}$Zn$_{0.8}$WO$_4$, Mg$_{0.3}$Zn$_{0.7}$WO$_4$, Mg$_{0.4}$Zn$_{0.6}$WO$_4$, ZnWO$_4$.

**Graph 2:**
- Light output, %
- ZnWO$_4$, Zn$_{0.1}$Mg$_{0.9}$WO$_4$, Zn$_{0.2}$Mg$_{0.8}$WO$_4$, Zn$_{0.3}$Mg$_{0.7}$WO$_4$, Zn$_{0.4}$Mg$_{0.6}$WO$_4$, Zn$_{0.5}$Mg$_{0.5}$WO$_4$, Zn$_{0.6}$Mg$_{0.4}$WO$_4$, Zn$_{0.7}$Mg$_{0.3}$WO$_4$, Zn$_{0.8}$Mg$_{0.2}$WO$_4$, Zn$_{0.9}$Mg$_{0.1}$WO$_4$, MgWO$_4$.

I. Tupitsina, D. Spassky, 2013
Private communication
Mixed oxides, (Ce,La)PO$_4$

Excitation spectra of solid solution (Ce,La)PO$_4$ at Ce absorption area and its intensity vs Ce concentration
Mixed oxides, silicates - LGSO:Ce

Excitation spectra of 400 nm luminescence at T=300K.

Important! The best efficiency of carrier multiplication and transfer to luminescence centers corresponds to 50:50 Gd:Lu rate

Ratio of intensities I(30 eV)/I(7 eV) of Ce1 (400 nm) and Ce2 (530 nm) excitation.

See details - O.Sidletskiy – O2.5
Mixed oxides, silicates - LGSO:Ce

Light yield in LGSO:Ce crystals with monoclinic C2/c structure vs. host composition

Oxides, garnets – GAGG and YAGG

Gd$_3$(Al$_x$Ga$_{1-x}$)$_5$O$_{12}$:Ce

(KAGG)


Y$_3$(Al$_x$Ga$_{1-x}$)$_5$O$_{12}$:Ce

(YAGG)

Scintillation yield and radioluminescence intensity dependence for mixed YAGG

Mixed oxides - YAGG:Ce

Energy storage in mixed YAGG:Ce scintillators

TSL (Thermo luminescence) for YAGG:Ce

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>YAG: Ce</td>
<td>102</td>
<td>1.17</td>
</tr>
<tr>
<td>YAGG (40%Ga):Ce</td>
<td>80</td>
<td>1.02</td>
</tr>
<tr>
<td>YAGG (60%Ga):Ce</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Ga doping allows to decrease the energy storage in YAGG comparing to YAG:Ce crystals
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$_x$La$_{1-x}$F$_3$

LaCl$_3$-LaBr$_3$

(Lu, Y)AlO$_3$: Ce

LGSO:Ce

Zn$_x$Mg$_{1-x}$WO$_4$

Gd$_2$(Al$_x$Ga$_{1-x}$)$_5$O$_{12}$:Ce

Ca$_{1-x}$Sr$_x$S

YAGG:Ce

Light output, %

X-ray

Zn$_{0.6}$Mg$_{0.4}$WO$_4$

Zn$_{0.5}$Mg$_{0.5}$WO$_4$

Zn$_{0.7}$Mg$_{0.3}$WO$_4$

Zn$_{0.9}$Mg$_{0.1}$WO$_4$

ZnWO$_4$
Thank you for your attentions!