Novel scintillation screen with significantly improved radiation hardness and very high light output

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4th generation family hold incorporated company (founded in 1934) with long tradition in handling and application of luminous material.

**DIVISIONS**

**WATCH INDUSTRY**
- Phosphorescent Pigment, Paint
- Varnish
- Accessories, Tools
- Measurement
- Application

**ISOTOPE TECH**
- Labelled Compounds
- Manifold Systems
- Sources
- Isotope Trading
- Decontamination
- Neutron Scintillation Screens

**SECURITY**
- Phosphorescent Thermoplastics
- Phosphorescent Paint
- Safety Panels
- Application (Instruments etc.)
- Fluorescent Paint
In 2005-2006 development of thin (50 - 100 micrometer) neutron sensitive scintillation screens on the basis of $^{6}\text{LiF}/\text{ZnS}$ for the PSI

After success in 2006 sales of this kind of screens to the market

Since 2014 distribution of scintillation screens on the basis of $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ and $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}/^{6}\text{LiF}$ for high resolution measurements

Since 2016/17 sales of PP/\text{ZnS}-scintillation screens for imaging with fast neutrons (see different presentations within WCNR-11 Malgorzata / Robert Zboray / ...) (Thank you James Hunter for initiation!!!)

*And from now: We will see within this presentation...*
Neutron Scintillation Screens

Typical digital camera system:

Scintillation Screen (two step mechanism):

- Core reaction with ions of high capture cross section ($^{155/157}\text{Gd}$, $^6\text{Li}$ or $^{10}\text{B}$) to create a secondary radiation.
- Excitation of a luminous material showing a fluorescence emission in the optimal range of the detection system.
The fluorescence mechanism:

1) Excitation creating a hole in the valence band and an excited electron in the conduction band
2) Relaxation of the excited electron to the ground level of the conduction band
3) Relaxation of the created hole to the top of the valence band
4) Fluorescence emission via an «impurity ion»
5) Non-emittive recombination of the electron and hole
6) Like 5) but via an impurity (defect center or impurity ion)

Fig. 2 Principle of scintillation in activated wide band gap materials.
Light yield:

\[ Y_{ph} = \frac{10^6 SQ}{\beta E_g} \text{ photons/MeV} \]

\( Y_{ph} \) = number of photons emitted by the scintillator per unit of energy absorbed

\( \beta \) = constant that appears approximately 2.5

\( E_g \) = band gap energy

\( S \) = transfer efficiency

\( Q \) = quantum efficiency

*For the ideal situation \( S \) and \( Q \) are 100%*
Degradation of ZnS:Cu/$^6$LiF scintillation screen during irradiation:

From Sept. 2015 to Sept. 2017:
CTI funded development project with PSI

Reason for degradation?
- Binder?
- Converter?
- Phosphor?
- Environment?

Fitting of the curve show a two fold exponential decay
Core reaction and secondary radiation given by the absorbing ions:

$^6$Li (Capture cross section [b] = 941):

$^6$Li + $^1$n $\rightarrow$ $^3$H + $^4$He + 4.79 MeV

Inorganic material used for the scintillator: $^6$LiF

$^{10}$B (Capture cross section [b] = 3838):

$^{10}$B + $^1$n $\rightarrow$ ($^{07\%}$) $^7$Li + $^4$He + 2.78 MeV

$^{10}$B + $^1$n $\rightarrow$ ($^{93\%}$) $^7$Li$^*$ + $^4$He + 2.30 MeV $\rightarrow$ $^7$Li + $^4$He + $\gamma$ (0.48 MeV)

Inorganic material used for the scintillator: $^{10}$BN, $^{10}$B$_2$O$_3$

$^{155/157}$Gd (Capture cross section [b] = 60900/254000):

$^{155}$Gd + $^1$n $\rightarrow$ $^{156}$Gd + $\gamma$ + conversion electrons (7.9 MeV)

$^{157}$Gd + $^1$n $\rightarrow$ $^{158}$Gd + $\gamma$ + conversion electrons (8.5 MeV)

Inorganic material used for the scintillator: Gd$_2$O$_2$S:Tb
The “Phosphor”

Similarity and difference of the colour centres creation under Y-quanta and hadrons

Point defects due to crystal growth

- $V_A$
- $V_C$
-Interstitial sites

Stars created by fission products

Set of isotopes identified in PWO crystal: measured activity 4 months after irradiation and the extrapolated values at 24 h and 7 months after the end of irradiation.

Point defects and their clusters which are created by knocked ions

Van Lint 1980

L.T. Chadding, 1965

M. Huhtienen 2001

Slide presented at SCINT 2017 conference in Chamonix by Korjik
Different phosphors show different radiation hardness:

FMAB peak efficiency and (1/e) decay dose rankings

<table>
<thead>
<tr>
<th>Scintillator coating</th>
<th>Peak efficiency</th>
<th>(1/e) decay dose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ratio</td>
<td>Rank</td>
</tr>
<tr>
<td>ZnS</td>
<td>Ag</td>
<td>1.00</td>
</tr>
<tr>
<td>YAG</td>
<td>Ce</td>
<td>0.31</td>
</tr>
<tr>
<td>Gd$_2$O$_2$S</td>
<td>Pr</td>
<td>4.70</td>
</tr>
<tr>
<td></td>
<td>Tb</td>
<td>2.13</td>
</tr>
<tr>
<td></td>
<td>Eu</td>
<td>6.14</td>
</tr>
<tr>
<td>Y$_2$O$_2$S</td>
<td>Tb</td>
<td>1.73</td>
</tr>
<tr>
<td></td>
<td>Eu</td>
<td>7.15</td>
</tr>
</tbody>
</table>

Two main effects are responsible for the degradation:

I) High energy irradiation or ions create a high density of disorder / vacancies in the crystal
   Effect by the disorder / vacancies / traps:
   a) Vacancies / disorder: increase of radiationless decay
   b) New traps: long decay
   c) Change in the surrounding of the emission center: Change in quantum efficiency

II) High energy irradiation force a high reactivity of the surface with the environment (O₂)
    a) Change of surface chemistry destroys the luminous mechanism (radiationless decay)
    b) The presence of oxygen in the ZnS matrix increase the migration of Cu
Different secondary irradiations / protection by varnish:

#19 → Standard mixture with $^6\text{LiF}/\text{ZnS}$
Relative $I(0)$: 100%

#20 → Mixture with $^{10}\text{B}_2\text{O}_3$
Relative $I(0)$: 18%

#24 → Standard $^6\text{LiF}/\text{ZnS}$ mixture with high quantity of varnish
Relative $I(0)$: 35%
Avoid oxygen:

Degradation of ZnS-phosphor by electron beam in different gas media

Argon does not stop complete degradation but fast component (oxidation process of the surface)

Sum of above and further things to do to improve:

Reduction of mechanism 1:
- Use scintillator with wider band gap (but intrinsically reduced light yield)
- Use emission center emitting in the orange / red region
- Use phosphor with lowest possible impurities and disorder (high crystallinity)
- Change from Li-6 to B-10 or Gd, due to lower energetic secondary radiations (but reduced light output)
- Doping with different cations to suppress damage (self repair mechanism)

Reduction of mechanism 2:
- Avoid oxygen and other reactive gases to supress reaction with environment
Main Reasons for higher radiation hardness:

- Red emission shows in general higher radiation hardness and

- Red emission is more efficient with standard CCD camera system

- $^{113}\text{Cd}$ is generating conversion electrons, which are less destructive than triton and alpha particles from $^6\text{Li}$

- Protection against air (oxygen) by use of higher varnish quantity

- Use of less $^6\text{LiF}$ in the mixture (Reduction of penetration of the phosphor by alpha particles)
Main features:
- After some time of irradiation 50% higher light output!
- Similar resolution in comparison to the ZnS:Cu/6LiF scintillation screen
- Better neutron statistics due to Cd-absorption. $^{113}\text{Cd}$ (~13% abundancy) has neutron cross section of 20’000
- Fluorescence lifetime is strongly reduced (see next slide)

But:
- CdS is in the SVHC list (Reach, Cd causes cancer), Special precautions are required!

<table>
<thead>
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<th>Special types</th>
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<tbody>
<tr>
<td><strong>Base material</strong></td>
</tr>
<tr>
<td>6LiF / Zn(Cd)S:Ag</td>
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</table>
Fluorescence Lifetime

Luminosity decay measurement after UV illumination
(Pigment partially activated, Varian Spectrometer)

Standard scintillation screens for neutron imaging (some technical data):

<table>
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<tr>
<th>Base material</th>
<th>Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6\text{LiF} / \text{ZnS}:\text{Cu}$ (ratio 1 / 2)</td>
<td>~2 s</td>
</tr>
<tr>
<td>$^6\text{LiF} / \text{ZnS}:\text{Ag}$ (ratio 1 / 2)</td>
<td>~2 s</td>
</tr>
<tr>
<td>$^6\text{LiF} / \text{Zn(Cd)}S:\text{Ag}$ (ratio 1 / 3)</td>
<td>~50 ms</td>
</tr>
<tr>
<td>$\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$</td>
<td>~4 ms</td>
</tr>
<tr>
<td>$\text{Gd}_2\text{Al}_2\text{Ga}<em>3\text{O}</em>{12}:\text{Ce}$</td>
<td>~30 μs</td>
</tr>
</tbody>
</table>
Special types:

**Gd$_3$Al$_2$Ga$_3$O$_{12}$:Ce** → Very high resolution / very short fluorescence lifetime and response!

<table>
<thead>
<tr>
<th>Special types</th>
<th>Base material</th>
<th>Emission</th>
<th>Dimension</th>
<th>Thickness</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gd$_3$Al$_2$Ga$<em>3$O$</em>{12}$:Ce</strong></td>
<td>450 nm (blue)</td>
<td>up to 100 x 150 mm</td>
<td>10 up to 100 μm</td>
<td>Very high resolution and very short decay (&lt;30 μs)</td>
<td></td>
</tr>
</tbody>
</table>
We are open to help you in your developments for new types of scintillation screen!

Thank you very much for your attention and we are looking forward to a further or new long and strong collaboration!
Fast Neutrons

For imaging with fast neutrons a polypropylene plate filled with a ZnS-phosphor is used. The scintillation is also a two step process. First neutrons interact with the hydrogen atoms of the polypropylene plate to build up recoiled protons. Those excite the ZnS to give the corresponding detectable light.

For information on light output / gamma sensitivity / resolution please have a look on the poster from Malgorzata G. Makowska or presentation by Robert Zboray or have a look into J. Imaging 2017, 3(4), 60

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<th>Thickness</th>
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<tr>
<td>PP / ZnS:Cu (30%)</td>
<td>530 nm (green)</td>
<td>up to 450 x 450 mm</td>
<td>1.5 - 3 mm</td>
<td>High light output and good resolution</td>
</tr>
<tr>
<td>PP / ZnS:Ag (30%)</td>
<td>450 nm (blue)</td>
<td>up to 450 x 450 mm</td>
<td>1.5 - 3 mm</td>
<td>High light output and good resolution</td>
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**6LiF / ZnS-Scintillation screens**

**6LiF / ZnS-Scintillation screens (green emitting)**

<table>
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<th>Thickness / Intensity / Resolution</th>
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<tbody>
<tr>
<td>With higher thickness we get higher light output.</td>
</tr>
<tr>
<td>With lower thickness we get a better resolution.</td>
</tr>
</tbody>
</table>

At NEUTRA with different setup we have a 10 times higher light output...

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**Standard scintillation screens for neutron imaging with cold or thermal neutrons (0.12 – 100 meV):**

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<th>Emission</th>
<th>Dimension</th>
<th>Thickness</th>
<th>Comment</th>
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<tbody>
<tr>
<td>6LiF / ZnS:Cu (ratio 1 / 2)</td>
<td>530 nm (green)</td>
<td>up to 400 x 400 mm</td>
<td>50 up to 400 μm</td>
<td>High light output and high resolution</td>
</tr>
<tr>
<td>6LiF / ZnS:Ag (ratio 1 / 2)</td>
<td>450 nm (blue)</td>
<td>up to 400 x 400 mm</td>
<td>50 up to 400 μm</td>
<td>High light output and high resolution</td>
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</table>
Thickness / Intensity / Resolution
With higher thickness we get higher light intensity
With lower thickness we get a better resolution

Saturation in light output at ~30-40 μm. Absolute intensity ~1/10 of ZnS/LiF screen, but better resolution...

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<td>Gd$_2$O$_2$S:Tb</td>
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</table>
Addition of $^6\text{LiF}$ give 30-50% higher brightness with same resolution!!!

| Standard scintillation screens for neutron imaging with cold or thermal neutrons (0.12 – 100 meV): |
|---|---|---|---|---|---|
| Base material | Emission | Dimension | Thickness | Comment |
| Gd$_2$O$_2$S: Tb / $^6\text{LiF}$ (20%) | 447 / 549 nm (blue-green) | up to 100 x 150 mm | 10 up to 50 μm | Very high resolution with enhanced intensity |