Improving scintillating materials for medical imaging applications

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JNCO, July 4th-7th, 2011
**CONTEXT**

**Saint-Gobain**: development and commercialization of new medical imaging devices

**LCMCP**: experience modeling scintillation, characterization tools...

**Thesis work**: improve scintillating materials – Mechanisms & Properties

- **Lu$_{1.8}$Y$_{0.2}$SiO$_5$:Ce (LYSO:Ce) single crystals**
  - Medical applications: Positron Emission Tomography (PET)

- **Gd$_2$O$_2$S:Pr,Ce (GOS:Pr,Ce) ceramics**
  - Medical applications: Computed Tomography (CT)

- **(Lu$_{0.5}$Gd$_{0.5}$)$_2$O$_3$:Eu (LuGdO$_3$:Eu) ceramics**

**Goal**: - Understand scintillation mechanisms
  - Enhance performances (Light Yield, Response time...)

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I. Scintillating Materials for Medical Imaging

II. Improving LYSO:Ce single crystals for PET

III. Improving Gd$_2$O$_2$S:Pr and LuGdO$_3$:Eu ceramics for CT

Summary & Perspectives
I. Scintillating Materials for Medical Imaging

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Summary & Perspectives
Scintillation: How does it work?

Excitation
- X-rays
- $\gamma$-rays

Absorption
- X or $\gamma$

Luminescent Center
- Excited level
- Emission
- Ground state

Valence Band
- Absorption
- Conversion
- Emission

Conduction Band

Applications
- Security (Nuclear material detection at airports…)
- Oil Logging
- Dosimetry
- High Energy Physics (LHC, CERN Geneva - CH)
- Medical Imaging ($\gamma$ and X Tomography)
Medical imaging requirements

- Efficient absorption of the ionizing radiation
- High Light Yield (> 10,000 photons/MeV)
- Fast fluorescence (ns to ms)
- Transparency (at $\lambda_{\text{emission}}$)
- Minimal delayed luminescence (*afterglow*)

Some scintillating materials…

LYSO:Ce$^{3+}$

$5d-4f$

(420 nm)

LuGdO$_3$:Eu$^{3+}$

$4f-4f$

(610 nm)

Blurred images (left) are caused by afterglow
Main issues

- Electronic traps
- Deeper electronic traps

Scintillation

- Improving LYSO:Ce
- Improving Gd$_2$O$_2$S:Pr & LuGdO$_3$:Eu

Conduction

- Band
- Excited level
- Emission
- Ground state
- Valence Band

Luminescent Center

- Absorption
- X-rays
- $\gamma$-rays

-$X$ or $\gamma$

-$\Delta T$

Delayed Luminescence

- AFTERGLOW

Decreased Light Yield at 25°C

Thermoluminescence as characterization tool

Traps filling (X-rays @ 10 K) → Continuous Heating → Collected emission

- Trap properties ($\Delta E$, kinetic...)

X-ray source

Optical fiber

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Summary & Perspectives
Positron Emission Tomography (PET)

Crystals + Photomultiplier Tubes

Thermoluminescence of LYSO:Ce

At T > 300 K traps negatively impact Light Yield

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>λ_{emission} (nm)</th>
<th>Light Yield (Photons/MeV)</th>
<th>Energy Resolution (%)</th>
<th>Decay Time (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₄Ge₃O₁₂ (BGO)</td>
<td>7.13</td>
<td>480</td>
<td>8200</td>
<td>15%</td>
<td>300</td>
</tr>
<tr>
<td>LuAlO₃:Ce (LuAP:Ce)</td>
<td>8.3</td>
<td>365</td>
<td>11000</td>
<td>9%</td>
<td>60 + 600</td>
</tr>
<tr>
<td>(LuY)₂SiO₅:Ce (LYSO:Ce)</td>
<td>7.1</td>
<td>420</td>
<td>32000</td>
<td>8%</td>
<td>40              + afterglow</td>
</tr>
</tbody>
</table>
Trap identification\cite{1}

LYSO:Ce prepared with:
- Different oxygen content (Floating Zone Technique)
- Different dopant (Ce$^{3+}$, Tb$^{3+}$)

Traps:
- Depend on oxygen content during growth
- Are not dopant-dependent

Oxygen vacancies:
Created during Czochralski (CZ) growth (industrial technique)
→ CZ requires LOW OXYGEN CONTENT (Iridium crucible, 2100°C)

\cite{1} Blahuta S. et al., Materials 2011, 4, 1224-1237 – Special Issue
Decreasing trap activity (1/2)

Effect of annealing on trap concentration

**Annealed in oxidizing conditions**
(1500°C/48h in air)
Reduced TL intensity: some oxygen vacancies are filled

**Annealed in reducing atmosphere**
(1200°C/12h in Ar+5%H₂)
Increased TL intensity: some oxygen vacancies are created

**Limited trap activity decrease by annealing**

Low impact on scintillation properties
Decreasing trap activity (2/2)

Oxygen vacancies → 2+ (energetically favorable): $V_{O^{**}}$

**Goal:** reduce their electron affinity

**How:** by adding a co-dopant: Ca$^{2+}$, Mg$^{2+}$

**Confirmation by TL:**
- 8 times less with Mg$^{2+}$
- 19 times less with Ca$^{2+}$

**Confirmation by Light Yield values:**
28000 → 33000 Ph/MeV with Mg$^{2+}$
28000 → 34000 Ph/MeV with Ca$^{2+}$
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Summary & Perspectives
Computational Tomography (CT)

| Scintillation | Improving LYSO:Ce | Improving Gd$_2$O$_2$S:Pr & LuGdO$_3$:Eu |

| X-ray source | Ceramics + photodiodes |

Afterglow: critical property

- Usually caused by traps with TL ~300 K
- LuGdO$_3$:Eu → Reduce traps with TL ~300 K
- Gd$_2$O$_2$S:Pr

Two methods for afterglow reduction

![TL Intensity vs Temperature](image)

<table>
<thead>
<tr>
<th>Density</th>
<th>$\lambda_{emission}$ (nm)</th>
<th>Light Yield (Photons/MeV)</th>
<th>Afterglow (ppm@3ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LuGdO$_3$:Eu</td>
<td>8.4</td>
<td>610</td>
<td>70000</td>
</tr>
<tr>
<td>Gd$_2$O$_2$S:Pr</td>
<td>7.0</td>
<td>495</td>
<td>20000</td>
</tr>
<tr>
<td>Gd$_2$O$_2$S:Pr,Ce</td>
<td>7.5</td>
<td>514</td>
<td>35000-50000</td>
</tr>
<tr>
<td>(Y,Gd)$_2$O$_3$:Eu,Pr</td>
<td>5.9</td>
<td>610</td>
<td>42000</td>
</tr>
<tr>
<td>CaWO$_4$</td>
<td>7.0</td>
<td>495</td>
<td>20000</td>
</tr>
</tbody>
</table>

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Electronic traps in Gd$_2$O$_2$S ceramics: Sulfur vacancies

S atoms $\rightarrow$ LAYER structure

**Sulfur vacancies**: lowest formation energy
- Created during very reducing processes
- Positively charged $\rightarrow$ electron traps

Light Yield at 25°C not impacted by traps\(^\text{[2]}\)

Afterglow can be reduced by:
- Codoping $\rightarrow$ LY also reduced!
- Sulfur annealing

$\rightarrow$ 1\(^{\text{st}}\) attempt: SO$_2$, no pressure (LY: +7%)
$\rightarrow$ 2\(^{\text{nd}}\) attempt: S, pressure

LuGdO$_3$:Eu,RE – co-doping for afterglow reduction

Luminescence mechanism:

$$Eu^{3+} + e^- \rightarrow Eu^{2+} \stackrel{h^+}{\rightarrow} (Eu^{3+})^* \rightarrow Eu^{3+} + h\nu$$

$$Trap + h^+ \rightarrow Trap^+ \stackrel{\Delta T}{\rightarrow} Trap + h^+ \quad \text{Afterglow}$$

RE$^{3+}$ co-dopants for efficient h$^+$ trapping

- No Light Yield reduction
- Doesn’t work with Ca$^{2+}$ or Zr$^{4+}$
**LYSO:**Ce single crystals
- Oxygen vacancies identified as the main electron traps
- Positive but limited effect of oxidizing post-treatment on traps
- Ca\(^{2+}/Mg^{2+}\) co-doping reduces trap activity and improves LY

**Gd\(_2\)O\(_2\)S:**Pr,Ce ceramics
- Sulfur vacancies are responsible for efficient electron trapping → Afterglow
- Traps may be removed by appropriate annealing (S, SO\(_2\)…)
- Gd\(_2\)O\(_2\)S:**Pr,Ce light yield is not impacted by traps

**LuGdO\(_3\):Eu,**RE ceramics
- Efficient afterglow reduction with Ce\(^{3+}\), Tb\(^{3+}\) and Pr\(^{3+}\) co-doping
- Good agreement between TL (trap concentration) and afterglow
- Efficient ceramics for X-ray Tomography
Thank you for your attention