Specificity and Response of the Photoluminescence of Irradiated Nanophosphors

*Topic Per4-G: Nanoscale Radiation Indicators (Thrust 5)*

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Grand Challenge

To detect radiation exposure remotely, long after the exposure occurred and discreetly. The detection should be sensitive to dose and specific to the type of radiation.

Project Scope

Test the photoluminescence (PL) of thermographic phosphors (TGP) before and after irradiation and (hopefully) identify a correlation between radiation displacement damage and PL emission.
Alternative title: *Non-scintillator radiation detection using nanophase phosphors*

Consider existing research in the area:

- Radiation in phosphors (mostly scintillators)
- Radiation effects in nanocrystals
- Radiation effects nano-phosphors (very few)
- Luminescence in nanophase phosphors
- **Radiation-induced *damage detection* using luminescent nanophase phosphors**

- There are very few articles (none?) in the literature that consider radiation-induced displacement damage in nano-phosphors.
CdSe nanocrystals

increasing 1 MeV proton dose

\[
\ln\left(\frac{PL}{PL_0}\right) = \text{dose } \left(10^{15} \text{ cm}^{-2}\right)
\]

<table>
<thead>
<tr>
<th>NC size (nm)</th>
<th>theoretical $\sigma_{NC} (\text{Å}^2)$</th>
<th>experimental $\sigma_{NC} (\text{Å}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>1.14</td>
<td>5.19</td>
</tr>
<tr>
<td>4.8</td>
<td>0.11</td>
<td>2.58</td>
</tr>
</tbody>
</table>

(R.C. Feldman, unpublished, used with permission)
Background and significance (2/3)

1. Naturally inert materials, so environmental effects (“in the field”) won’t alter phosphor’s response to radiation exposure

2. Fabrication is easy and scalable, so mass production will be likely if the right material can be designed.

3. Doping can tune properties to control sensitivity range, response characteristics, excitation frequency, luminescence, etc.

4. Indefinite shelf life

5. Once damage occurs, the material will contain a record of the damage essentially indefinitely.

6. Response can be queried at a distance.

7. We have a good deal of experience with these materials, so we have a basis for comparison.
Background and significance (3/3)

- **YAG**: screening material because we already have a great deal of experience and understanding of its characteristics. This will allow us to establish a robust experimental protocol.

<table>
<thead>
<tr>
<th>Material</th>
<th>Molecular mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>YAG (Y_3\text{Al}<em>5\text{O}</em>{12})</td>
<td>593</td>
</tr>
<tr>
<td>YGG (Y_3\text{Ga}<em>5\text{O}</em>{12})</td>
<td>807</td>
</tr>
<tr>
<td>LAG (\text{Lu}_3\text{Al}<em>5\text{O}</em>{12})</td>
<td>851</td>
</tr>
<tr>
<td>LGG (\text{Lu}_3\text{Ga}<em>5\text{O}</em>{12})</td>
<td>1066</td>
</tr>
</tbody>
</table>

- **Pyrochlores**: experience plus larger stopping power, which should provide more sensitivity to radiation. Plus fabrication technique produces smaller particles.

  \[
  A_2B_2O_7 \\
  \text{A–site} \\
  \begin{array}{c|c|c|c}
  \text{La} & \text{Nd} & \text{Eu} \\
  \hline
  4\%\text{Eu} & 4\%\text{Eu} & 4\%\text{Eu} \\
  \end{array}
  \]

- **Strontium alumina**: readily available, doped with boron. Boron is known to have an exceptionally large cross-section, so interaction with radiation should also be quite large.
Technical Approach (1/1)

• To determine the (I) spectral photoluminescence modification of (II) nanophase (III) YAG, pyrochlores and strontium alumina doped with boron as a function of size when exposed to (IV) x-rays, protons, alphas and neutrons.

I
– Relative intensity
– Decay time/quenching
– Peak shift

II
– separation technologies
– size distribution
– synthesis options

III
– change doping levels to adjust molecular weight (radiation cross-section)
– characterization

IV
– vary energy, dose rate and dose to find thresholds of sensitivity

• Results will provide selectivity and sensitivity of selected rare earth phosphors in radiation environments.
Results—Nano-sizing techniques

- TEM gives us reason to believe we have nanocrystallites.
- Nano-sizing the samples
  - Filter: TFF filters capable of filtering 200 nm and 500 nm particles have been used. No particles were seen below 200 nm. Few particles below 500 nm.
  - Separation: Need a better way to break up airy foam from combustion synthesis (ball milling)
  - Direct fabrication: Thermochemical analysis for designing combustion control
    * mass-controlled reactor
    * thermochemical properties of the precursor at various steps in combustion are needed
    * TGA/DSC/MS has been performed to study these values
Results—Thermochemical analysis

TGA-DSC for lanthanum zirconate (pyrochlore) made with glycine (fuel):

- Initial mass loss and heat flow is water evaporation
- Initial endothermic reaction unknown
- Combustion temperature is 282°C (accompanied by a mass loss).
- Decrease in mass is due to residual combustion products cooking off

- Combustion parameters lead to better combustion processes
Results—Simulation

- SRIM provides penetration depths and stopping powers for materials selection and experimental design

MRED

SRIM

LAMMPS

Marlowe
Results—x-ray irradiation

We saw no change in the luminescence, decay time, XRD, XPS, ...

- However, this was expected. X-rays are ionizing and (in general) do not create physical damage.
- We used these tests to prove out our mounting system and characterization techniques.
Results—proton irradiation of $\text{La}_2\text{Zr}_2\text{O}_5$

Evidence of damage is less than 1 week old

Pyrochlore sample was irradiated to a fluence of $2 \times 10^{15} \text{cm}^{-2}$

- Physical appearance changed: discolored (yellowish gray) spot where beam struck the sample

- Could be damage as in oxygen vacancies in yttrium oxide
- Could be carbon buildup on sample surface
Results—proton irradiation of La$_2$Zr$_2$O$_5$

- decrease in red emission when illuminated with UV (PL)

<table>
<thead>
<tr>
<th>pre</th>
<th>post</th>
</tr>
</thead>
</table>

- beam was $D = 3$ mm, which is commensurate with the apparent damage
- extraction of “red” channel shows a decrease in color that corresponds to the beam impact site. No corresponding decrease in green or blue channels.
Results—proton irradiation of La$_2$Zr$_2$O$_5$

- cathodoluminescence (CL) appears to degrade with time

- the green channel of one pixel from the series of images was collected and plotted.
- The fit is a standard exponential

\[ I = I_0 \exp \left( -\frac{t}{\tau} \right) + I_{\text{off}} \]

\[ I_0 = 150; \quad \tau = 47 \text{ min}; \quad I_{\text{off}} = 130. \]
Results—proton irradiation of La$_2$Zr$_2$O$_5$

- PL significantly altered after $\Phi = 2 \times 10^{15} \text{cm}^{-2}$

![Graph showing PL intensity vs. wavelength](image)

- relative peaks shift—this is important because it suggests that the degradation is not due to contamination on the surface
- background increase in blue region—could be Eu$^{3+}$ $\rightarrow$ Eu$^{2+}$ resulting from displacement damage because Zr has similar oxidation states
Accomplishments

- Publications: abstracts to MRS and NSREC
- Presentations: 2 abstracts for AVS meeting in Nashville
- Students (supported at various levels):
  - Sarah Gollub (Materials Science, PhD 2014)
  - Justin Collar (Materials Science, REU summer 2011)
  - Stephanie Weeden-Wright (Electrical Engineering, PhD 2014)
  - Bobby Harl (Chemical Engineering, PhD 2013)
  - Rachael Hansel (Mechanical Engineering, postdoc)
Conclusions

- Ceramic rare-earth phosphors are viable candidates for stand-off, discrete, delayed, radiation sensors.
Future Directions

• Immediate goals (next year)
  – Step-stress tests on pyrochlore and YAG with protons
  – Vary concentration of gallium substituted YAG for subsequent proton testing
  – alternative pyrochlore configurations
  – detailed simulations of damage in our compounds
  – non-isotopic alpha sources

• Long-term (one year away)
  – neutrons
  – boron-based phosphors
  – effects of nano-particle size
### Eu$^{3+}$ transitions

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>E 25500</th>
<th>5D3 24200</th>
<th>5D2 21500</th>
<th>5D1 19000</th>
<th>5D0 17200</th>
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<tbody>
<tr>
<td>7F0</td>
<td>0</td>
<td>392</td>
<td>413</td>
<td>465</td>
<td>526</td>
</tr>
<tr>
<td>7F1</td>
<td>400</td>
<td>398</td>
<td>420</td>
<td>474</td>
<td>538</td>
</tr>
<tr>
<td>7F2</td>
<td>1000</td>
<td>408</td>
<td>431</td>
<td>488</td>
<td>556</td>
</tr>
<tr>
<td>7F3</td>
<td>1900</td>
<td>424</td>
<td>448</td>
<td>510</td>
<td>585</td>
</tr>
<tr>
<td>7F4</td>
<td>2500</td>
<td>435</td>
<td>461</td>
<td>526</td>
<td>606</td>
</tr>
<tr>
<td>7F5</td>
<td>3900</td>
<td>463</td>
<td>493</td>
<td>568</td>
<td>662</td>
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<tr>
<td>7F6</td>
<td>4800</td>
<td>483</td>
<td>515</td>
<td>599</td>
<td>704</td>
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## Radiation sources

<table>
<thead>
<tr>
<th>type</th>
<th>source</th>
<th>energy</th>
<th>beam</th>
</tr>
</thead>
<tbody>
<tr>
<td>x-ray</td>
<td>Aracor 4100</td>
<td>10 keV</td>
<td>3 cm</td>
</tr>
<tr>
<td>proton</td>
<td>Van de Graaff</td>
<td>$\leq 1.8$ MeV</td>
<td>3 mm, 1 cm scan</td>
</tr>
<tr>
<td>gamma</td>
<td>$^{60}$Co</td>
<td>1.33 MeV &amp; 1.17 MeV</td>
<td>isotopic</td>
</tr>
<tr>
<td>alpha</td>
<td>$^{241}$Am</td>
<td>3.4 MeV in air</td>
<td>1.5 cm$^2$ isotopic</td>
</tr>
<tr>
<td>heavy ion</td>
<td>tandem pelletron</td>
<td>1 – 4 MeV</td>
<td>5 $\mu$m</td>
</tr>
<tr>
<td>neutron</td>
<td>ORNL (SNS/HFIR)</td>
<td>tbd</td>
<td>tbd</td>
</tr>
</tbody>
</table>
## Schedule

### Irradiation matrix

<table>
<thead>
<tr>
<th></th>
<th>YAG/YGG</th>
<th>Pyrochlores</th>
<th>SA:boron*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>x-rays</strong></td>
<td>Y1</td>
<td>Y1</td>
<td>Y2</td>
</tr>
<tr>
<td><strong>protons</strong></td>
<td>Y1</td>
<td>Y1</td>
<td>Y2</td>
</tr>
<tr>
<td><strong>alphas</strong></td>
<td>Y1</td>
<td>Y1</td>
<td>Y2</td>
</tr>
<tr>
<td><strong>neutrons</strong></td>
<td>Y3</td>
<td>Y3</td>
<td>Y3</td>
</tr>
<tr>
<td><strong>other</strong></td>
<td>Y3</td>
<td>Y3</td>
<td>Y3</td>
</tr>
</tbody>
</table>

* strontium alumina doped with boron
The text reads:

**What are thermographic phosphors?**

- Materials that emit light when excited and whose emission is temperature dependent
- Usually ceramics doped with rare earth elements
- Not to be confused with phosphorus
- Excitation can be light, electrons, x-rays

**Uses**

- TV screens/CRT
- Plasma display
- Fluorescent lighting
- Glow-in-the-dark toys

**Thermal measurement**

- Decay time
- Relative intensity peaks
- Line shift
TGP Fabrication

Normally, fabrication involves diffusional process that 1) is time consuming, 2) requires lots of thermal energy, 3) is difficult to control, and 4) requires post-processing to get luminescence.

Combustion synthesis

1. Mix nitrates of constituents stoichiometrically with urea
2. Heat in a muffle furnace or hot plate for a few minutes
3. Calcining can improve emission

Materials

- Gallium-substituted YAG:Ce $(Y_{1-x}Ce_x)_3(Al_{1-y}Ga_y)_{5}O_{12}$. Widely used in solid-state lighting and lasers.
- Pyrochlores $(A_2B_2O_7)$ Used as thermal barrier coating
Combustion products
• Hypothesis: small crystallites provide more surface states that increase non-radiative pathways for altered spectra and decay times.
• This effect appears not to be an issue for crystallites larger than 20 nm, which is what we get.
Materials design

Dieke diagram

Configurational coordinate diagram

Absorption

Fluorescence

\[ E \]

\[ E_{pi} \]

\[ E_1 \]

\[ E_0 \]

\[ q_i \]

\[ q_{i0} \]

\[ \hbar \Omega_i \]
YAG:Ce Characterization

Red shift with gallium in \((Y_{1-x}Ce_x)\_3(Al_{1-y}Ga_y)\_5O_{12}\)

<table>
<thead>
<tr>
<th>(x) (%Ce)</th>
<th>(y) (%Ga)</th>
<th>(\lambda_{em}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0</td>
<td>537</td>
</tr>
<tr>
<td>0.01</td>
<td>0.5</td>
<td>514</td>
</tr>
<tr>
<td>0.02</td>
<td>0</td>
<td>539</td>
</tr>
<tr>
<td>0.02</td>
<td>0.5</td>
<td>517</td>
</tr>
</tbody>
</table>

Decay mechanisms

Multi-phonon emission

Temperature-dependent decay has a radiative and non-radiative component.

\[ \frac{1}{\tau} = P_r + P_{nr} \]

Weber’s model for non-radiative recombination

\[ P_{nr}(T) = P_{nr}(T = 0) \left[ 1 - \exp\left( \frac{E_{ph}}{k_B T} \right) \right]^{-n} \]

Results of fit to pyrochlore data

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_{ph} ) (cm(^{-1}))</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(<em>{1.92})Eu(</em>{0.08})Zr(_2)O(_7)</td>
<td>785</td>
<td>24</td>
</tr>
<tr>
<td>La(<em>{1.92})Eu(</em>{0.08})Hf(_2)O(_7)</td>
<td>745</td>
<td>21</td>
</tr>
</tbody>
</table>
YAG:Ce Results

- $x$ is the percent gallium
- gallium red-shifts the emission and decreases the decay time
Pyrochlore Results

**Excitation**

[Graph showing excitation spectra for different compounds with intensity on the Y-axis and wavelength on the X-axis.]

**Emission**

[Graph showing emission spectra for different compounds with intensity on the Y-axis and wavelength on the X-axis.]

**Lifetime**

[Graph showing lifetime versus temperature for different compounds with lifetime on the Y-axis and temperature on the X-axis.]