Luminescent materials for dosimetric applications

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Basic assumption: There is a relation between:

- **light yield**
- **absorbed dose**
Steps in TL Dosimetry

1. Irradiation
2. Storage
3. Read-out
Steps in OSL Dosimetry

Luminescent material

γ, X-rays, e⁻, p, HCP

Ionisation

Storage

Read-out

laser

λ_{stimulation} > λ_{emission}

Q1: How is it energetically possible that E_{em} > E_{stim}?
Which luminescent material is a good dosimetric material?

- Application area
- Type of radiation
- Type of dosimetry
Application areas

• Personnel dosimetry
  • Extremity
  • Whole body

• Environmental dosimetry
  • Terrestrial
  • Space

• Medical dosimetry
  • Radiotherapy
  • Diagnostic radiology
  • Nuclear medicine

• High dose dosimetry
  • Radiation processing
  • Nuclear reactors
Type of radiation

- Low LET radiation
  - photons
  - betas
  - electrons

- High LET radiation
  - protons
  - Heavy Charged Particles (HCP)
  - neutrons

- UV radiation
Type of Dosimetry

- **Passive**
  - Thermoluminescence Dosimetry (TLD)
  - Optically Stimulated Luminescence Dosimetry (OSLD)
  - Electron Paramagnetic Resonance (EPR)
  - Film Dosimetry

- **Active**
  - Fiber optic dosimetry

General requirements

- Sensitivity
- Linearity
- Appropriate energy dependence
  - independence radiation energy
  - tissue equivalent
- Long term stability
- Reproducible
- Easy to re-set, low residual
Specific requirements

- Match luminescence spectrum with maximum sensitivity of PM tube
- Mechanically strong
- Chemically inert
- No effect of day light (for TL)
- Radiation resistant
- Batch homogeneity
- Simple reuse
- Low production price
Application areas

Dose range (Gy)

- Personnel dosimetry \(10^{-5} - 0.5\)
  - Extremity
  - Whole body

- Environmental dosimetry \(10^{-7} - 10^{-2}\)
  - Terrestrial
  - Space

- Medical dosimetry
  - Radiotherapy \(10^{-1} - 100\)
  - Diagnostic radiology \(10^{-6} - 10^{-1}\)
  - Nuclear medicine

- High dose dosimetry
  - Radiation processing \(10^1 - 10^6\)
  - Nuclear reactors \(10^3 - 10^9\)
Application areas

<table>
<thead>
<tr>
<th>Dose range (Gy)</th>
<th>Uncertainty 1SD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^{-5} – 0.5</td>
<td>-30, +50</td>
</tr>
<tr>
<td>10^{-7} – 10^{-2}</td>
<td>±30</td>
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<tr>
<td>10^{-1} – 100</td>
<td>?</td>
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<tr>
<td>10^{-6} - 10^{-1}</td>
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<tr>
<td>10^{1} - 10^{6}</td>
<td>15</td>
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<tr>
<td>10^{3} - 10^{9}</td>
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Q2: Which uncertainty is required in radiotherapy?
### Application areas

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<td>• Radiotherapy</td>
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<tr>
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<td>-30, +50</td>
<td>+</td>
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| Environmental dosimetry 10^{-7} – 10^{-2} | ±30 | ++ |
| Terrestrial |
| Space |

| Medical dosimetry |
| Radiotherapy 10^{-1} – 100 | 3.5 | + |
| Diagnostic radiology 10^{-6} - 10^{-1} | 3.5 | + |
| Nuclear medicine |

| High dose dosimetry |
| Radiation processing 10^1 - 10^6 | 15 | - |
| Nuclear reactors 10^3 - 10^9 | | |
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</table>
Tissue equivalence for Photons

\[
D_{TL} = \Phi E (\mu_{en}/\rho)_{TL} \quad (1)
\]

\[
D_{tissue} = \Phi E (\mu_{en}/\rho)_{tissue} \quad (2)
\]

From (1) and (2):

\[
\frac{D_{TL}}{D_{tissue}} = \frac{(\mu_{en}/\rho)_{TL}}{(\mu_{en}/\rho)_{tissue}}
\]
Tissue equivalence for neutrons

\[ D \approx K = \Phi E \left( \frac{\mu_{tr}}{\rho} \right) \]

\[ \frac{K}{\Phi} = E \left( \frac{\mu_{tr}}{\rho} \right) \]

\[(NH_4)_2BeF_4:Ti^+\]

\[(NH_4)_2SiF_6:Ti^+\]
Luminescence efficiency

How efficiently transform TL/OSL materials absorbed energy into light?

\[ \eta_i = \frac{\text{energy emitted}}{\text{energy absorbed}} \]

\[ = \frac{N_{\text{photons}} \ h \nu}{mD} \]
Luminescence phenomena, applications and typical efficiencies

<table>
<thead>
<tr>
<th>Type of luminescence</th>
<th>Induced by</th>
<th>Application</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black body radiation</td>
<td>Heat</td>
<td>Tungsten filament lamp</td>
<td>~5%</td>
</tr>
<tr>
<td>Photoluminescence</td>
<td>Photons</td>
<td>Fluorescent lamp</td>
<td>~20%</td>
</tr>
<tr>
<td>Cathodoluminescence</td>
<td>Electrons</td>
<td>Television screen</td>
<td>~10%</td>
</tr>
<tr>
<td>Electroluminescence</td>
<td>Electric field</td>
<td>LED, flat panel display</td>
<td>0.1-50%</td>
</tr>
<tr>
<td>Thermoluminescence</td>
<td>Ionising radiation</td>
<td>Dosimetry, Dating</td>
<td></td>
</tr>
</tbody>
</table>

Q3: \( \eta_{TLD-100} \) ?

A: 0.01%
B: 0.10%
C: 1.0%
D: 10%
Steps in the energy conversion process

- creation of electron-hole pairs ($n_{eh} \sim E_{\gamma}/W_{eh} = h\nu/\beta E_g$)
- thermalisation and trapping ($\eta_{tr}$)
- release of charge carriers from the trap ($p$)
- transfer to luminescent centre ($S$)
- de-excitation of the Luminescent Centre ($Q$)
- escape from the sample ($\eta_{esc}$)

$$\eta_i = \frac{h\nu}{\beta E_g} \eta_{tr} p S Q \eta_{esc}$$
Luminescence efficiency

\[ \eta_i = \frac{h\nu}{\beta E_g} \eta_{tr} \ p \ S \ Q \ \eta_{esc} \]

Suppose: \( \eta_{tr} = 1, p = 1, S = 1, Q = 1, \eta_{esc} = 1 \)

\[ \eta_{i,\text{max}} = \frac{h\nu}{\beta E_g} \]
### $\eta_{i,\text{max}}$ and $\eta_{\text{exp}}$ for some TL materials

<table>
<thead>
<tr>
<th>TL material</th>
<th>$E_g$ (eV)</th>
<th>$\beta$</th>
<th>$h\nu$ (nm)</th>
<th>$\eta_{i,\text{max}}$ (%)</th>
<th>$\eta_{\text{exp}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF:Mg,Ti</td>
<td>13.6</td>
<td>1.7</td>
<td>410</td>
<td>3.02</td>
<td>13</td>
</tr>
<tr>
<td>LiF:Mg,Cu,P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaF$_2$:Dy(TLD-200)</td>
<td>12.6</td>
<td>1.8</td>
<td>480</td>
<td>2.58</td>
<td>11</td>
</tr>
<tr>
<td>CaF$_2$:Cu,Ho</td>
<td>12.6</td>
<td>1.8</td>
<td>390</td>
<td>3.18</td>
<td>14</td>
</tr>
<tr>
<td>CaF$_2$:Tm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaF$_2$:Mn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KMgF$_3$:Ce</td>
<td>12.6</td>
<td>2</td>
<td>360</td>
<td>3.44</td>
<td>14</td>
</tr>
<tr>
<td>BeO</td>
<td>10.6</td>
<td>2</td>
<td>335</td>
<td>3.70</td>
<td>17</td>
</tr>
<tr>
<td>CaSO$_4$:Dy</td>
<td>9.5</td>
<td>2</td>
<td>575</td>
<td>2.16</td>
<td>11</td>
</tr>
<tr>
<td>CaSO$_4$:Mn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$:C</td>
<td>8.7</td>
<td>2.7</td>
<td>420</td>
<td>2.95</td>
<td>13</td>
</tr>
<tr>
<td>Li$_2$B$_4$O$_7$:Mn</td>
<td>8.5</td>
<td>2</td>
<td>620</td>
<td>2.00</td>
<td>12</td>
</tr>
<tr>
<td>C (diamond)</td>
<td>5.5</td>
<td>2.9</td>
<td>498</td>
<td>2.49</td>
<td>16</td>
</tr>
</tbody>
</table>

**Average**

| $\sim$13 | $\sim$1 |
**Efficiency various steps**

- creation e-h pairs \( \sim 13\% \)
- trapping (\( \eta_{tr} \)): ?
- release of charge carriers from the trap (p): ++
- transfer to luminescent centre (S): - +
- de-excitation of the Luminescent Centre (Q): - +
- escape from the sample (\( \eta_{esc} \)): +

**Conclusion:**

The trapping efficiency plays a dominant role in the overall efficiency.
Well known TL/OSL materials

- LiF family
- CaSO\(_4\):RE (RE = Dy, Tm, Sm)
- CaF\(_2\):Mn
- Li\(_2\)B\(_4\)O\(_7\):Mn
- MgB\(_4\)O\(_7\):Dy, Na
- Al\(_2\)O\(_3\):C
- BeO
- SrS:Ce, Sm

Q4: Which class of materials do **not** show TL?
LiF family

- LiF: Mg, Ti
  - Patent 1963
  - Thermo Electron (TLD-100, TLD-600, TLD-700)
  - TLD Poland: LiF:MT

- LiF: Mg, Cu, P
  - First mentioned by Nakajima et al. 1978
  - SSDL, Beijing, China: GR200
  - Nemoto, Japan, NTL-500
  - Thermo Electron: TLD100H
  - TLD Poland: LiF:MCP
Glow curves LiF

Dose response

\[ f(D) = \frac{TL(D)}{D} \left/ \frac{TL(D_0)}{D_0} \right. \]

Linear: \( f(D) = 1 \)
supralinear: \( f(D) > 1 \)
sublinear: \( f(D) < 1 \)

# Role of dopants

<table>
<thead>
<tr>
<th>LiF:Mg,Ti</th>
<th>LiF:Mg,Cu,P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg: 0.01 – 0.02%</td>
<td>Mg: 0.2%</td>
</tr>
<tr>
<td>Ti: 10 – 15 ppm</td>
<td>P: 1 – 4%</td>
</tr>
<tr>
<td></td>
<td>Cu: 0.02 -0.5%</td>
</tr>
</tbody>
</table>

**Anneal procedure**

- 1 h 400 °C
- 24 h 80 °C
- 10 min @240 °C
TLD cycle

- Annealing procedure
- Storage and irradiation
- Post-irradiation anneal
- Readout
Glow curve TLD-100 after storage
Requirements OSL material

- Sensitivity
- Trapping centres:
  i) Thermally stable
  ii) Optically accessible
- Good separation between emission and stimulation bands
- Dose erasure by optically bleaching
1 mW laser: $10^{17}$ photons cm$^{-2}$ s$^{-1}$
OSL-signal: $< 10^6$ photons cm$^{-2}$ s$^{-1}$

Q5: What is the role of the colour filter?
**Al₂O₃:C**

- before 1990: Al₂O₃ known as TL material
- 1990: anion-deficient Al₂O₃:C developed as high sensitive TL material
- 1995: OSL material

Application in
- Personnel dosimetry
- Environmental dosimetry
- Retrospective dosimetry
- Dating applications (equivalent to quartz)

**Q6: What is the role of C?**

A: Trapping centre

B: Luminescent centre

C: None of both
Emission and stimulation spectra of Al$_2$O$_3$::C

\[ e^- + F^+ \rightarrow F^* \rightarrow F + h\nu_{420 \text{ nm}} \]

OSL-signal of Al2O3:C

\[ \lambda_{\text{stimulation}} = 470 \, \text{nm} \]

[Graph showing OSL signal (a.u.) vs. Time (s) for different doses (0 mGy, 1 mGy, 2 mGy, 4 mGy, 7 mGy, 15 mGy, 30 mGy).]
Dose response


Kodak XV-2 film

120 kVp
280 kVp
60Co
6MV photons
20 MeV electron

Source:

Environmental dosimetry

BeO

- Known for a long time as TL material
  (used in routine personnel dosimetry by the ENEA-Italy dosimetry service)
- Relatively low TL sensitivity
- Strong TL self-absorption
- Strong supralinearity
- Highly tissue equivalent;
  \[ Z_{\text{eff}}(\text{BeO}) = 7.2 \; ; \; Z_{\text{eff}}(\text{tissue}) = 7.4 \]
- Rediscovered as OSL material (Bulur, Sommer et al.)
BeO: OSL dose response

BeO Batch 5

OSL signal (counts/channel)

Integrated luminescence (counts)

Time (s)

Dose (mGy)
BeO: dose response

BeO batch 5

Integrated Luminescence (counts)

Dose (mGy)

Integrated Luminescence (counts)

Dose (Gy)

- TL (130 - 360 °C)
- OSL (9 - 509 s)

- Batch 5 (OSL: 0 - 250 s)
- Batch 5 (TL: 100-300 °C)
Cu⁺ doped fused quartz

MgO:Tb$^{3+}$

$\lambda_{\text{stimulation}} = 470$ nm

Irradiation: $^{90}$Y/$^{90}$Sr

$\text{OSL signal (arb. units)}$

$\text{Time (s)}$

$\text{Dose (mGy)}$

$\text{Integrated OSL signal}$
MgO:Tb$^{3+}$: Fading

The graph shows the normalized signal of OSL, TL peak 1+2, and TL peak 3 over time and temperature. The y-axis represents the normalized signal, while the x-axis represents time in hours. The inset graph illustrates the temperature in degrees Celsius against the normalized signal. The data points indicate the fading behavior of the MgO:Tb$^{3+}$ material under fading conditions.
SrS:Ce,Sm

\[ \lambda_{\text{stimulation}} = 1.04 \, \mu m \]

Irradiation: UV (350 nm)

SrS:Ce,Sm comparison with Al$_2$O$_3$:C

- Emission and stimulation bands are well separated
- No deep traps, SrS is fully reset after reading
- Strong fading

Benoit et al. University of Montpellier, France
Chemical Vapor Deposition (CVD) Diamond

Attractive features:

• Tissue equivalent
• Chemical inertness
• Radiation hardness
• Physically robust
• Safe for *in vivo* use
Chemical Vapour Deposition Diamond

Source: Goncalves et al Optical Materials  27(2005)1231
Problems with CVD Diamond

- Fading of the TL signal
- Sensitivity to daylight
- Poor linearity
- Poor reproducibility
Concluding remarks

• The development of new dosimetric materials goes slowly
• The market is dominated by LiF and Al₂O₃
• Even of well-known dosimetric materials the exact mechanism is unknown
• The key issue in developing an improved dosimetric material is
  a high concentration of stable trapping centres
  that can be synthesized in a reproducible way