Thermoluminescence and Defect Structure of $\text{Eu}^{2+}$ and $\text{Mn}^{2+}$ doped $\text{BaMgAl}_{10}\text{O}_{17}$

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Outline

• Application areas of BAM

• Crystal structure and luminescence spectra of BAM

• Problem setting

• Thermoluminescence analysis
  – BAM:Eu
  – BAM:Mn

• Interpretation and conclusions
Application Areas of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu(Mn)}$

Fluorescent Lamps

Plasma Displays

High photoluminescence efficiency and perfect color point for tricolor lamps and emissive displays
Structure of BaMgAl_{10}O_{17} (BAM)

Eu^{2+} occupies Ba^{2+} sites in the conduction layers
Mn^{2+} occupies Mg^{2+} sites in the spinel blocks
Luminescence Spectra of BAM:Eu and BAM:Mn

Excitation and reflection spectra

<table>
<thead>
<tr>
<th>Wavelength [nm]</th>
<th>Reflection [%]</th>
<th>Quantum efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>250</td>
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<td></td>
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<tr>
<td>300</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

LO = QE(1-R)

Band gap (host lattice) 4f5d (Eu$^{2+}$)

Excitation bands: 170 nm (host lattice)
230 nm (4f5d Eu$^{2+}$)
320 nm (4f5d Eu$^{2+}$)

Emission band: 453 nm (5d4f Eu$^{2+}$)
515 nm (5d5d Mn$^{2+}$)
Problem Setting

Change of spectral light output

Time dependence of light output

Strong degradation during device operation related to
- $\text{Eu}^{3+}$ formation
- Powder quality (crystallinity) and Ba/Mg/Eu/Al ratio
Thermoluminescence Analysis
first order (monomolecular) TL kinetics

\[ I_{TL} = N_{T_0} s \exp\left(-\frac{E}{kT}\right) \cdot \exp\left[-\frac{s}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{kT}\right) dT \right] \]

- \( N_{T_0} \): number of trapped electrons
- \( s \): decay frequency
- \( b \): heating rate
- \( E \): energy trap depth below excited state

Randall, Wilkins 1945
Thermoluminescence Analysis

first order (monomolecular) TL kinetics

\[ I_{TL} = N_{T_0} s \exp\left(-\frac{E}{kT}\right) \cdot \exp\left[\frac{s}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{kT}\right) dT\right] \]

\[ \frac{dI_{TL}}{dT} = 0 \quad \text{at} \quad T = T_m \]

\[ \frac{\beta \cdot E}{k \cdot T_m^2} = s \cdot \exp\left(-\frac{E}{kT_m}\right) \]
Thermoluminescence Analysis of BAM:Eu

Annealing in air at 500°C

TL intensity decreases
Peak structure does not change
High temperature band shows up
Thermoluminescence Analysis of BAM:Eu

Annealing in air or Nitrogen

Annealing in air
• Density of shallow traps decreases

• Density of deep trap (0.3 eV) increases

Annealing in Nitrogen
• Deep trap does not show up
Thermoluminescence Analysis of BAM:Eu

Annealing in $N_2$ or $N_2/H_2$

Annealing in Nitrogen
- Density of shallow traps decreases

Annealing in $N_2/H_2$
- Density of shallow traps decreases again
- Deep trap does not show up
Light Output of BAM:Eu

Annealing in N$_2$ or N$_2$/H$_2$ at 700°C

Annealing in Nitrogen
Reduces its efficiency over the complete wavelength range

Annealing in N$_2$/H$_2$
Restores initial efficiency
Thermoluminescence Analysis of BAM:Eu

Thermoluminescence vs. Excitation Wavelength

- Shallow trap structure is independent of excitation energy.
- Deep trap glow peak only due to low energy excitation ($\lambda > 180$ nm).
- TL is most intense under band gap excitation.
Thermoluminescence Analysis of BAM:Mn

Comparison between BAM:Eu and BAM:Mn

BAM:Mn exhibits similar peak structure than BAM:Eu

trap levels are lattice and not activator related
Thermoluminescence Analysis of BAM:Mn

BAM:5%Mn

TL-intensity is 2.2 times higher than for BAM:Eu
Trap depth energy is 0.04 eV smaller than for BAM:Eu
Thermoluminescence Analysis of BAM:Mn

BAM:5%Mn - thermal treatment in air

Light output for $\lambda < 170$ nm slightly increases
TL fine structure remain unchanged $\Rightarrow$ trap structure unchanged
TL fine structure intensity unchanged $\Rightarrow$ trap density unchanged
Interpretation of TL Spectra of BAM

Annealing experiments

• In air at 500°C
  – reduction of shallow trap density due to diffusion (within the conduction layers)
  – Formation of oxygen vacancies due to annealing in N₂/H₂ during synthesis
  – oxidation of Eu²⁺ to Eu³⁺ (trap at 0.3 eV, color centre), not for Mn²⁺

• In N₂ at 500°C
  – reduction of oxygen vacancy density due to diffusion
  – no oxidation of Eu²⁺

• TL spectrum after annealing in N₂/H₂ at 500 or 700°C
  – Increase of oxygen vacancy density due to removal of Oxygen

TL spectra dependent on excitation energy

• Photon energy >> band gap: band excitation and efficient ET to Eu²⁺
• Photon energy ~ band gap: exciton formation and electron trapping on defects
• Photon energy < band gap: 4f5d excitation of Eu²⁺
Thermoluminescence Model for BAM

Shallow traps are located in the band gap, 0.1 to 0.2 eV below the excited state of Eu$^{2+}$ and Mn$^{2+}$.
Conclusions

Light output reduction and deep trap formation (0.3 eV) only occur in presence of Oxygen (only for BAM:Eu) ⇒ related to Eu$^{3+}$ formation

Annealing in reducing atmosphere improves VUV light output and deep traps disappear (reduction of Eu$^{3+}$ to Eu$^{2+}$)

⇒ Degradation of BAM:Eu is largely caused by oxidation of the redoxsensitive activator Eu$^{2+}$