Raw materials for novel complex oxide garnet scintillators development

G. Dosovitskiy

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Problem: strong phosphorescence in GGAG:Ce crystals

Excitation by 440nm LED 1 min after excitation

- Co-doping with Mg diminish phosphorescence, but simultaneously decreases light yield of scintillation;
- A special effort has to be spend to define the origin of the mechanism of phosphorescence in multicomponent garnet;
- Suppression of phosphorescence has a potential for future increase of light yield of GGAG:Ce;
- Success in this direction can give an additional tool to engineer new multicomponent scintillation materials.

Background of random coincidences at scintillation kinetics measurements by start-stop method is due to phosphorescence in the material.
**September - High-Purity Holmium Oxide / Ho2O3 / Rare Earth**

Zhongshan Malrich Magnetic & Hard... Discount | Free Inspection

US $1-99 / Kilogram
1 Kilogram (Min. Order)

Contact Supplier

**September - Multifunctional rare earth product praseodymium**

Inner Mongolia Hualite Import & Export Co., Ltd.

Discount | Free Inspection

5 Tons (Min. Order)

Contact Supplier

**September - Rare Earth Compound 99.99% Holmium Oxide**

Ganzhou Wanfeng Advanced Materials...

US $38-50 / Kilogram
1 Kilogram (Min. Order)

Contact Supplier

**Erbium oxide, Er2O3, rare earth oxide powder from China, high purity**

Xiamen Mirai Material Technology Co., Ltd.

US $50-100 / Kilogram
1 Kilogram (Min. Order)

Contact Supplier

**September - Nano rare earth oxide Lanthanum oxide La2O3**

Shanghai Runsheng Chemical Technol...

Discount | Free Inspection

US $10-1000 / Kilogram
100 Kilograms (Min. Order)

Contact Supplier

**September - high purity rare earth oxide powder Ce2O3, cerium oxide powder**

Shanghai Kessen Ceramics Co., Ltd.

Discount | Free Inspection

US $1-2 / Kilogram
2 Kilograms (Min. Order)

Contact Supplier

**High purity 99.9% rare earth oxide powder Y2O3**

Jiangsu Yongchao Magnetic Materials...

US $6.5-8 / Kilogram
50 Kilograms (Min. Order)

Contact Supplier

**High purity 99.99% rare earth oxide powder Yttrium Oxide Pr...**

Qingdao Xiguanya International Trade Co., Ltd.

US $3-5 / Kilogram
1 Kilogram (Min. Order)

Contact Supplier
Raw materials parameters

\[ \text{e.g. for Gd}_{3-x}\text{Ce}_x(\text{Ga,Al})_5\text{O}_{12} \]

- **Purity**
  - + 10-100 ppm Mg, Cr, Yb, ...
  - impurity defects
  - influence on growth or sintering

- **Composition**
  - Gd\(_{3-x}\)Ce\(_x\)(Ga,Al)\(_5\)O\(_{12}\)
  - additional phases
  - non-stoichiometry defects

- **Microstructure**
  - Crystallite size,
  - agglomerate size and strength
  - grain size
  - optical quality

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**Single crystals**

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**Powders, ceramics**
Different concentrations of impurities
examples of solutions

Coloring impurity
KMnO₄ in water

ppm
- 0.1 1 10 100

Mechanical impurity
YAG nanopowder suspension in water

ppm
- 1 10 100 1000
Raw materials purity:

Initial components + additional purification + processing impurities

Grading: 99.99% = 100% - Σ(All controlled impurities)

\( \text{Y}_2\text{O}_3 \) 99.99% (4N) from well known suppliers:

<table>
<thead>
<tr>
<th>Product Number:</th>
<th>11181</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS number:</td>
<td>1314-36-9</td>
</tr>
<tr>
<td>MDL number:</td>
<td>MFCD00011473</td>
</tr>
<tr>
<td>Molecular formula:</td>
<td>( \text{O}_3\text{Y}_2 )</td>
</tr>
<tr>
<td>Linear formula:</td>
<td>( \text{Y}_2\text{O}_3 )</td>
</tr>
<tr>
<td>Molecular weight:</td>
<td>225.81</td>
</tr>
</tbody>
</table>

| CAS Number | 1314-36-9 |
| Molecular Weight | 225.81 |

<table>
<thead>
<tr>
<th>TEST</th>
<th>SPECIFICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>APPEARANCE (COLOR)</td>
<td>White</td>
</tr>
<tr>
<td>APPEARANCE (FORM)</td>
<td>Powder</td>
</tr>
<tr>
<td>TITRATION (KT) EDTA 0.1M</td>
<td>77.6 - 79.9 % Y</td>
</tr>
</tbody>
</table>

| PURITY | ≥ 99.99 % Based On Rare Earth Analysis |
| X-RAY DIFFRACTION | CONFORMS TO STRUCTURE |
| ICP ANALYSIS | Confirms Yttrium Component |
| METAL TRACE ANALYSIS (ICP) | ≤ 200 PPM (Trace Rare Earth Analysis) |
99.99% = 100% - Σ(All **controlled** impurities)

Y$_2$O$_3$ 99.99%  ICP mass-spectrometry analysis

Precise control of impurities is needed

**Insufficient purity – low performance**

**Excess purity – high costs**
Spectral overlaps in atomic emission spectrometry

- **Gd – 0.1 wt.%**
- **Ti – $10^{-5}$ wt.% (solutions)**

Line 323.45 nm

Line 334.94 nm

Line 336.12 nm

Equal to 100 ppm Ti in Gd

2D CID detector image

Spectrum representation

iCAP 6300 Duo spectrometer, Thermo Scientific
Mass spectrometry of Gd$_2$O$_3$ 5N

All usable Yb isotopes are overlapped with GdO$^+$ and GdOH$^+$ ions.

Tb and Lu are also overlapped.

“Complicated” compounds require combination of the two techniques.
## Developed impurity specifications

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Limit</th>
<th>Negative influence</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>5 ppm</td>
<td>Radiation hardness</td>
<td>→ Pb</td>
</tr>
<tr>
<td>K</td>
<td>2 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>1 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>5 ppm</td>
<td>Scintillation kinetics</td>
<td>→ Pb</td>
</tr>
<tr>
<td>Ba</td>
<td>3 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>5 ppm</td>
<td>Radiation hardness, robustness</td>
<td>→ W</td>
</tr>
<tr>
<td>3d (Ti-Ni)</td>
<td>0,5 ppm</td>
<td>Scintillation kinetics</td>
<td>→ W</td>
</tr>
<tr>
<td>Fe</td>
<td>2 ppm</td>
<td>Radiation hardness</td>
<td>→ W</td>
</tr>
<tr>
<td>Cd</td>
<td>5 ppm</td>
<td>Scintillation kinetics</td>
<td>→ Pb</td>
</tr>
<tr>
<td>Sb</td>
<td>5 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RE (La-Lu)</td>
<td>Not natural</td>
<td>Radiation hardness, scintillation kinetics</td>
<td>→ Pb</td>
</tr>
</tbody>
</table>
Qualitative effects of impurities could be studied on powders

Example - YAG:Ce photoluminescence

Alkaline metals

Alkaline earth metals

Photoluminescence intensity

Impurity content, mol.%

K
Na
Li

Mg
Ca

0,001        0,01         0,1           1

0,001        0,01         0,1           1
**COMPOSITION**

\[ \text{Gd}_{3-x}\text{Ce}_x(\text{Ga,Al})_5\text{O}_{12} \] – disordered crystalline solid solution

<table>
<thead>
<tr>
<th></th>
<th>Gd(^{3+})</th>
<th>Ga(^{3+})</th>
<th>Al(^{3+})</th>
<th>Ce(^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R(_i), pm</strong></td>
<td>119,3</td>
<td>76/61</td>
<td>53/67,5</td>
<td>128,3</td>
</tr>
<tr>
<td>Oxygen coordination</td>
<td>8</td>
<td>6, 4</td>
<td>4, 6</td>
<td>8</td>
</tr>
</tbody>
</table>

Crystal ionic radii

- Difference of ionic radii of Al and Ga predetermines a distortion of the lattice or even accumulation of the distortions;
- Systematic deficiency of one of the cations also can create systematically present defect;
- Both, systematic distortions and systematic defects may be involved in the phosphorescence mechanism

In a GGG-GAG solid solution a predominant evaporation of the Ga is expected while crystal pulling from the crucible (Czochralski method).
Demand for a synthesis of the raw material. Powder production by precipitation.

Solid state synthesis – risk of inhomogeneity

“Wet chemical” routes: Co-precipitation, sol-gel, pyrolysis – use chemically homogenized precursors

Powder for measurements:
- homogeneous composition
- homogeneous microstructure
- dense $\mu$m range particles

Advantages of co-precipitation:
- High uniformity material
- Composition control and scalability
Precipitate microstructure

Lack of precipitant

NH$_4$OH relative to stoichiometric quantity

Lack of Ga

Ga Ok

Gel-like precipitate formed of 10-20 nm particles

EDX maps

Precipitate microstructure

2 μm

10 μm

100 nm

5 μm

16
Room temperature luminescence and luminescence excitation spectra of the powder material sintered at 1600°C

No significant influence of the raw material stoichiometry variation on the luminescent properties of sintered GGAG:Ce was detected.
Scintillation kinetics dependence on composition

### $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}:\text{Ce}(1\ \text{at.\%})$

<table>
<thead>
<tr>
<th></th>
<th>$\tau_1$, ns</th>
<th>$P_1$, %</th>
<th>$\tau_2$, ns</th>
<th>$P_2$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1% Ga</td>
<td>48</td>
<td>81%</td>
<td>108</td>
<td>19%</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>79%</td>
<td>117</td>
<td>21%</td>
</tr>
<tr>
<td>-1% Ga</td>
<td>41</td>
<td>59%</td>
<td>82</td>
<td>41%</td>
</tr>
<tr>
<td>~5% Ga</td>
<td>42</td>
<td>67%</td>
<td>132</td>
<td>33%</td>
</tr>
<tr>
<td>~5% Ga</td>
<td>47</td>
<td>72%</td>
<td>177</td>
<td>28%</td>
</tr>
</tbody>
</table>

### $\text{Gd}_3\text{Ga}_{2.8}\text{Al}_{2.2}\text{O}_{12}:\text{Ce}(1\ \text{at.\%})$

<table>
<thead>
<tr>
<th></th>
<th>$\tau_1$, ns</th>
<th>$P_1$, %</th>
<th>$\tau_2$, ns</th>
<th>$P_2$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1% Ga</td>
<td>39</td>
<td>54%</td>
<td>68</td>
<td>46%</td>
</tr>
<tr>
<td></td>
<td>47</td>
<td>86%</td>
<td>125</td>
<td>14%</td>
</tr>
<tr>
<td>-1% Ga</td>
<td>39</td>
<td>62%</td>
<td>77</td>
<td>38%</td>
</tr>
<tr>
<td>~5% Ga</td>
<td>42</td>
<td>66%</td>
<td>111</td>
<td>35%</td>
</tr>
<tr>
<td>~5% Ga</td>
<td>45</td>
<td>71%</td>
<td>119</td>
<td>29%</td>
</tr>
</tbody>
</table>

At the relatively large Ce content the ratio between scintillation kinetics components is weakly dependent of the stoichiometry variation.
Strong Ga deficiency leads to some phosphorescence

$\text{Gd}_3\text{Ga}_{2.85}\text{Al}_2\text{O}_{12} : \text{Ce (1 at.%)}$

- 42 ns (67%)
- 132 ns (33%)

$\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12} : \text{Ce (1 at.%)}$

- 37 ns (79%)
- 117 ns (21%)

Phosphorescence contribution
Raw materials for PWO crystals

Influence of stoichiometry on radiation hardness

PbO : WO$_3$ evaporate from a melt at rates 60 : 40

Deviation from stoichiometry accumulates each crystallization

R$^2 = 0.1291$

> 900 crystals measurement data from production

Source: $^{60}$Co, $10^4$ rad/h
Irradiation time: 20 min
Hold before measurement: 8 h
MICROSTRUCTURE

Nanopowders for ceramics

Primary particles
Size, Form

Agglomerates
Size, hardness

Scintillation powders
Grain and pores structure
Primary particles morphology effect on ceramics microstructure

Example - $\text{Y}_2\text{O}_3$
Agglomeration in raw material powder has effect on ceramics density
Agglomeration control

For highly polydisperse powders microscopy give only qualitative information.

Direct observation
SEM, optical microscopy

Informative
Persuasive
Small sample volumes (could be unrepresentative)

\[ \text{Tb}_3\text{Al}_5\text{O}_{12} \]
Agglomeration control

Indirect methods
laser diffraction
light scattering
surface absorption
sedimentation

Express and/or cheap
Representative probes
0,1g ≈ 10^5 particles

Method must be
adjusted to every
individual product

Measurements series 3 months

Laser diffraction
Measurement after 0-2-4-6, min.:
Co-doping effect on primary particle size

YAG:Ce + ~1% B

1100 °C

1600 °C
Grain size of the powder affects luminescence

Scintillation ($\alpha$, 5.5 MeV)

Reference single crystal

Photoluminescence

Sintering $T$, $^\circ C$

Int., a.u.

$\lambda$, nm

$0.25$

$0.2$

$0.15$

$0.1$

$0.05$

$0.0$

$450$ $500$ $550$ $600$ $650$ $700$ $750$

$1500$ $1200$ $1000$ $900$ $C$

$1000$ $C$

$1200$ $C$

$1500$ $C$

$10 \mu m$

$500$ nm

$10 \mu m$

$500$ nm

$10 \mu m$

$500$ nm
Crystallinity increases phosphorescence in $\text{Gd}_3\text{Ga}_{3-\Delta}\text{Al}_2\text{O}_{12}:\text{Ce}$ (1 at.%).

1200 °C

$1 \mu\text{m}$

Counts

37 ns (56%)
80 ns (32%)
173 ns (12%)

1600 °C

$1 \mu\text{m}$

Counts

45 ns (68%)
128 ns (32%)

Phosphorescence contribution
Conclusions

Impurities content, composition, microstructure – factors, which influence properties of garnet scintillators – take origin on raw materials preparation stage.

Appropriate techniques should be chosen for raw materials control.

Pre-characterization of properties of garnet materials could be done using powders, however there are limits: e.g., powder microstructure could influence measured properties, such as phosphorescence level.

Attention from a raw material preparation stage and feedback throughout a material development / production chain could help to improve materials. Approach successfully tested on PWO crystals development.
Thank you for your attention!!!

Many thanks to my colleagues:


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