新規無機単結晶シンチレーターの実用化開発

鎌田　圭

New Industry Creation Hatchery Center (NICHe),
Tohoku University, Sendai, 980-8579, Japan

Kamada@imr.tohoku.ac.jp
The history of scintillators starts short after the discovery of X-rays at the end of the 19th century...

W.C. Roentgen, Science 3, 227 (1896)

ON A NEW KIND OF RAYS.*

1. A discharge from a large induction coil is passed through a Hittorf’s vacuum tube, or through a well-exhausted Crookes’ or Lenard’s tube. The tube is surrounded by a fairly close-fitting shield of black paper; it is then possible to see, in a completely darkened room, that paper covered on one side with barium platinocyanide lights up with brilliant fluorescence when brought into the neighborhood of the tube, whether the painted side or the other be turned towards the tube. The fluorescence is still visible at two metres distance. It is easy to show that the origin of the fluorescence lies within the vacuum tube.

CaWO₄ powder in 1996

Year of introduction of a scintillation material
<table>
<thead>
<tr>
<th></th>
<th>Ti: NaI</th>
<th>Ti: CsI</th>
<th>BGO</th>
<th>Ce: LYSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ( \text{g/cm}^3 )</td>
<td>3.67</td>
<td>4.53</td>
<td>7.13</td>
<td>7.1–7.2</td>
</tr>
<tr>
<td>Decay time ( \text{ns} )</td>
<td>230</td>
<td>1050</td>
<td>300</td>
<td>40</td>
</tr>
<tr>
<td>Hygropcopicity</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Light yield ( \text{photon/MeV} )</td>
<td>45000</td>
<td>56000</td>
<td>8000</td>
<td>30000</td>
</tr>
<tr>
<td>E.R. ( % @ 662\text{keV} )</td>
<td>5.6</td>
<td>5.7</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>m.p., ( \text{℃} )</td>
<td>651</td>
<td>621</td>
<td>1050</td>
<td>2050</td>
</tr>
<tr>
<td>Wavelength ( \text{nm} )</td>
<td>415</td>
<td>550</td>
<td>480</td>
<td>420</td>
</tr>
<tr>
<td>Selfradiation</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>
What is the recent trend for the development of high performance scintillator?

1. Fine tuning of well-known materials
   i. Band gap engineering;
      Pr:LuAG, Ce:GGAG,

2. Higher technology for elaboration
   i. Hygroscopic materials
      LaBr₃, CLYC, SrI₂, Cs₃RECl₆, CsRE₂Cl₇,
      CsBa₂I₅: Eu, BaBrI:Eu, ...
   ii. Incongruent materials
       LPS, GPS, ..
   iii. Eutectic scintillator

3. Prospective
Developing method

**Micro-pulling down method (μ-PD)**

- Laser, nonlinear
- Scintillator
- Piezoelectric
- Faraday rotator

**Czochralski (Cz) method**

- High quality bulk single crystal

Rapid materials screening by μ-PD and high quality big bulk growth by Cz

1 crystal / 5haors

Evaluation

Devices and applications
What is the recent trend for the development of high performance scintillator?

1. Fine tuning of well-known materials
   i. Band gap engineering;  
      \( \text{Pr:LuAG, Ce:GGAG,} \)

2. Higher technology for elaboration
   i. Hygroscopic materials  
      \( \text{LaBr}_3, \text{CLYC, Srl}_2, \text{Cs}_3\text{RECl}_6, \text{CsRE}_2\text{Cl}_7, \text{CsBa}_2\text{I}_5: \text{Eu, BaBrI:Eu, ...} \)
   ii. Incongruent materials  
       \( \text{LPS, GPS, ..} \)
   iii. Eutectic scintillator

3. Prospective
Scintillation properties of Pr:LuAG

$\text{Pr : Lu}_3\text{Al}_5\text{O}_{12}$

- It shows desirable properties such as fast decay time and high light yield.

In some host lattice Pr$^{3+}$ also exhibit 5d-4f luminescence like Ce$^{3+}$ and decay time can be even faster.

Radioluminescence spectra of Pr doped crystals at room temperature
Micro-pulling-down technology

<RF heating µ-PD furnace>

Quartz tube
Work coil
Ir crucible
After heater
Grown crystal
Alumina stage
Seed crystal

Grown crystals

\[ \text{Y}_3\text{Al}_5\text{O}_{12} (\text{YAG}) \text{ Pr} 0.25\% \]
\[ \text{Y}_3\text{Al}_5\text{O}_{12} (\text{YAG}) \text{ Pr} 1\% \]
\[ \text{Lu}_3\text{Al}_5\text{O}_{12} (\text{LuAG}) \text{ Pr} 0.25\% \]
\[ \text{Lu}_3\text{Al}_5\text{O}_{12} (\text{LuAG}) \text{ Pr} 1\% \]
Continuous Growth & Multi Growth techniques

- Available to control the shape of the crystals
- Continues materials supply
- High growth rate

\[ \text{Losses by cut & polish} \approx \text{less than 10\%} \]

\[ \text{Low Cost !!, Control of composition, segregation} \]

\[ \mu\text{-PD method} \]

Processing is not complicated

Low Cost !!, High Speed!!
Shaped crystal growth by micro-pulling-down method

YAG crystal (5mm□)

LuAG crystal (φ3mm)

Sapphire fiber

Fluoride crystal

Plate shaped sapphire

Plate shaped PrF₃

Sapphire plate and tube crystals

K₃Li₂Nb₅O₁₅ (KLN) plate crystal
Scintillation properties of Pr:LuAG

I(t) = 47exp[-t/23.46ns] +3exp[-t/96.8ns]

<table>
<thead>
<tr>
<th>Scintillators</th>
<th>Pr:LuAG (Lu₃Al₅O₁₂)</th>
<th>Ce:GSO (Gd₂SiO₅)</th>
<th>Ce:LYSO ((Lu,Y)₂SiO₅)</th>
<th>BGO (Bi₄Ge₃O₁₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>6.7</td>
<td>6.7</td>
<td>7.3</td>
<td>7.13</td>
</tr>
<tr>
<td>Light Yield (BGO=100)</td>
<td>20000</td>
<td>200</td>
<td>32000</td>
<td>8000</td>
</tr>
<tr>
<td>Decay Time (ns)</td>
<td>23(80%),97(20%)</td>
<td>40-60</td>
<td>30-40</td>
<td>300</td>
</tr>
<tr>
<td>Peak emission (nm)</td>
<td>310</td>
<td>430</td>
<td>420</td>
<td>480</td>
</tr>
<tr>
<td>Energy Resolution (%@662keV)</td>
<td>4.8 (10mm cubic)</td>
<td>8</td>
<td>9</td>
<td>12</td>
</tr>
<tr>
<td>Selfradiation</td>
<td>Lu</td>
<td>No</td>
<td>Lu</td>
<td>No</td>
</tr>
<tr>
<td>Cleavage</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>1970</td>
<td>1950</td>
<td>2150</td>
<td>1050</td>
</tr>
</tbody>
</table>
Scintillation properties in high temperature of Pr:LuAG

Pr:LuAG shows 40% higher light yield at 450K than room temperature

⇒ Oil logging application
Development of Pr:LuAG, radiation detector, PEM system and imaging properties test

November, 2004

Development of Pr:LuAG

4 inch is available!

Production stage

Machining and arraying

2-D imaging
(H8500-03, Hamamatsu)

March, 2009
PEM using Pr:LuAG

Imaging properties test using phantom

4 mm
10 mm
8 mm
6 mm
紫外高感度型APDアレー＋LuAGの評価

12x12 APD-arrey : pixel size = 2mm, pixel gap =0.25mm
8x8 APD-arrey : pixel size = 3mm, pixel gap = 0.25mm

12x12 Pr:LuAG-array : scintillator size=2.05x2.05x10mm³, thickness of reflector=0.20mm
UV-enhanced APD-array

Q.E. of UV-enhanced APD-array

- Conventional APD
- UV-enhanced APD single pixel type (Si resin window)
- UV-enhanced APD-array (Si resin window + surface optimization)

Q.E. = 53% @ 310 nm
Antisite defects in YAG and LuAG single crystals


Antisite defect is the most easy defect configuration in AG lattice. Their existence is confirmed by both theoretical and experimental results.

Exchange of Y(Lu) and Al ions is an inevitable consequence of the growth from high temperature melt.

We propose:

CB ——— Electron trap ——— VB
Scintillation decay at RT

After correlated TSL and EPR study the “design” of the key processes was proposed:

At RT

\[ \tau > 30 \mu s \]

Data from Chewpraditkul, IEEE TNS 56, 3800 (2009)

Consideration of tunneling-driven recombination provides a physical ground for the slower scintillation decay component in LuAG:Ce, which can’t be explained by thermal detrapping and recombination via conduction band as calculated detrapping times are too long.

\[ I(t) = 22.1 \exp(-t/63\text{ns}) + 6.47 \times 10^6 (93302 + 107061t)^{-1.31} + 0.000727 \]

Effect of Ga doping in Lu$_3$Al$_5$O$_{12}$

- LuAG:Pr
  - Ga0%
  - Ga10%
  - Ga20%

- LuAG:Ce
  - Ga0%
  - Ga10%
  - Ga20%

- undoped LuAG
  - Ga0%
  - Ga10%
  - Ga20%

LuAG

- Conduction band
- 0.29 eV
- >7 eV
- Valence band

LuGAG

- Conduction band
- Antisite
- Valence band

Fasoli et al., PRB 84 (2011)
Gd$_3$Al$_5$O$_{12}$ (incongruent)

By Ga$^{3+}$ substitution in Al$^{3+}$ site, Gd$_3$(Al,Ga)$_5$O$_{12}$ phase can be congruent.

μ-PD growth of Ce:(Gd,Y,Lu)$_3$(Ga,Al)$_5$O$_{12}$

In addition, we have tried La in Dodecahedral site, Lu, Sc, Mg, Zr, Hf, … in Octahedral site. Consequently, we found that **Ga substitution is the best** in this system.
Radioluminescence spectra measurements

Evaluations of radioluminescence spectra of Ce: (Lu,Gd)$_3$(Al,Ga)$_5$O$_{12}$ crystals (CuKα, R.T.)

![Graph showing RL peak intensity vs. Ga index](image)

Noticeably higher Stokes shift in Gd-rich samples is estimated from the Ce$^{3+}$ absorption and luminescence peak positions. While it is about 0.34 eV for Ce:LuAG, it is about 0.48 eV for Ce:Gd$_3$Al$_3$Ga$_2$O$_{12}$ and 0.50 eV for Ce:Gd$_2$Lu$_1$Al$_3$Ga$_2$O$_{12}$ compositions which show the highest RL intensity.

From the scintillation efficiency point of view the region of host compositions Gd$_2$-3Lu$_1$-0Al$_2$-3Ga$_3$-2O$_{12}$ is the most advantageous one.
2 inch growth of GAGG single crystal with various Ga concentrations

- Ga2.7 crystal showed single garnet phase in whole crystal.
- Ga2.4 crystal showed secondary prrovskite phase at the beginning part
- Ga2 crystal showed single garnet phase at only the end part
Energy spectra of Ce1%:GAGG

- Light yield
  (correction by Fe55 peak and QE of the APD: 80%@520nm, 70%@420nm)
  APD Hamamatsu S8664-55, shaping time: 2µS
- Sample size
  5x5x5mm (All face are mechanically polished)

  - The best light yield was around 60,000 photon/MeV in GAGG (Ga2.7).
  - The best Energy resolutions was 3.8%@662keV in GAGG (Ga2.0).
Ga dependence of important parameters part II

Ordered structure
\{Gd\}_3[Ga]_2(Al)_3O_{12}

Best BG

Band-gap energy (keV)

Energy resolution (%)

Light yield (10^4 ph/MeV)

\[ x \text{ in } \text{Gd}_3(\text{Ga}_x,\text{Al}_{1-x})\text{O}_{12} \]

Development of Ce:GAGG and its application

With Furukawa, JAEA, Univ. Tokyo

Nov. 2010

Ce:Gd₃(Al,Ga)₅O₁₂

development

Nov. 2011 in the market

Luminescent study, LY, Decay evaluation

Sept. 2012

Compact & real time Survey meter

Just one year

Detector unit

GAGG + APD

Food checking system

GAGG Compton camera on the unmanned helicopter

Jan. 2011

2inch crystal!

With Furukawa, JAEA, Univ. Tokyo
Development of Ce:GAGG and its application

3inch Ce1%:GAGG
(Ce0.03Gd2.97Ga3Al2O12)

0.5mm □ アレー
0.4mm □ アレー
0.2mm □ アレー
Gamma camera for $^{137}$Cs imaging

早大 片岡教授、浜松ホトニクス社
JST先端計測技術プログラム
携帯ガンマカメラの開発
(片岡研HPより)
Timing properties of GAGG

<table>
<thead>
<tr>
<th></th>
<th>Ce: GAGG</th>
<th>Ce: LYSO</th>
<th>Ti: NaI</th>
<th>Ti: CsI</th>
</tr>
</thead>
<tbody>
<tr>
<td>density g/cm³</td>
<td>6.7</td>
<td>7.1–7.2</td>
<td>3.67</td>
<td>4.53</td>
</tr>
<tr>
<td>Decay time ns</td>
<td>90–100</td>
<td>30–40</td>
<td>230</td>
<td>1050</td>
</tr>
<tr>
<td>Higroscopisity</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>L.Y. photon/MeV</td>
<td>56000</td>
<td>32000</td>
<td>45000</td>
<td>50000</td>
</tr>
<tr>
<td>E.R. %@662keV</td>
<td>5</td>
<td>9</td>
<td>5.6</td>
<td>5.7</td>
</tr>
<tr>
<td>m.p., °C</td>
<td>1800</td>
<td>2050</td>
<td>651</td>
<td>621</td>
</tr>
<tr>
<td>Wavelength nm</td>
<td>520</td>
<td>420</td>
<td>415</td>
<td>550</td>
</tr>
<tr>
<td>Self radiation</td>
<td>no</td>
<td>Yes (Lu)</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

- GAGG is chemically stable material and shows high light yield, high energy resolution without self radiation.

- However timing response is slower than LYSO

⇒ Improvement of timing response of GAGG is necessary in order to apply GAGG for positron emission tomography.
Improvement of timing response by Mg$^{2+}$ co-doped on Ce:GAGG

The stable Ce$^{3+}$ center is much less effective in such competition as it needs first to capture the hole from the valence band. Another advantage of Ce$^{4+}$ center is that the last step in its scintillation mechanism, the hole capture from valence band, must always be nonradiative, i.e. not contributing to an afterglow.
the radiation resistance of the sample set was tested under an X-ray irradiation (40 kV, 10 mA, 30 min, estimated dose 300 Gy) by the measurement of the induced absorption $IA(\lambda)$ evaluated from the equation

$$IA(\lambda) = \{Airr(\lambda) - A0(\lambda)\} \times 2.3/d(cm)$$

where $Airr(\lambda)$ and $A0(\lambda)$ are absorbance values after and before X-ray irradiation, respectively and $d(cm)$ is the sample thickness.
What is the recent trend for the development of high performance scintillator?

1. Fine tuning of well-known materials
   i. Band gap engineering; GGAG, GSAG, ...

2. Higher technology for elaboration
   i. Hygroscopic materials
      LaBr₃, CLYC, SrI₂, Cs₃RECl₆, CsRE₂Cl₇, CsBa₂I₅: Eu, BaBrI:Eu, ...
   ii. Incongruent materials
       LPS, GPS, ..
   iii. Eutectic scintillator

3. Prospective
High performance halide scintillator

Scintillation properties of LaBr$_3$:Ce$^{3+}$ crystals: fast, efficient and high-energy-resolution scintillators

E.V.D. van Loef$^a$, P. Dorenbos$^{a,*}$, C.W.E. van Eijk$^a$, K.W. Krämer$^b$, H.U. Güdel$^b$

$^a$ Radiation Technology Group, Interfaculty Reactor Institute, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands

$^b$ Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3000 Bern 9, Switzerland

Fig. 3. Pulse height spectrum of LaBr$_3$:0.5% Ce$^{3+}$ under $^{137}$Cs $\gamma$-ray excitation, recorded with a shaping time of 10$\mu$s. The inset shows part of the spectrum on a linear scale.
Halide scintillators

Table 1
Scintillation properties of Ba halides, Sr halides and CsI activated with Eu²⁺.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Luminosities</th>
<th>Decay time</th>
<th>Energy resolution</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaF₂</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>[6]</td>
</tr>
<tr>
<td>BaCl₂</td>
<td>19,400</td>
<td>390</td>
<td>8.8</td>
<td>[6]</td>
</tr>
<tr>
<td>BaBr₂</td>
<td>15,700</td>
<td>585</td>
<td>11</td>
<td>[6]</td>
</tr>
<tr>
<td>BaI₂</td>
<td>40,000</td>
<td>&lt; 1000</td>
<td>8</td>
<td>[7,8]</td>
</tr>
<tr>
<td>CsI</td>
<td>19,100</td>
<td>N/A</td>
<td>N/A</td>
<td>[9]</td>
</tr>
<tr>
<td>SrF₂</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>[9]</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>[9]</td>
</tr>
<tr>
<td>SrBr₂</td>
<td>25,000</td>
<td>N/A</td>
<td>8</td>
<td>[8]</td>
</tr>
<tr>
<td>SrI₂</td>
<td>80,000</td>
<td>1200</td>
<td>2.7</td>
<td>[10]</td>
</tr>
</tbody>
</table>


Fig. 1. Examples of polycrystalline samples packed in dry atmosphere in quartz cuvettes for optical characterization (top: room light; bottom: UV illumination).


Fig. 1. Single crystals of MgCl₂:Eu²⁺ grown by the vertical gradient freeze method. The crystal plate in the lower photograph is ~1 cm² in area and is illuminated with UV light in the lower right photograph.
We developed the moisture controlled $\mu$-PD furnace for the growth of halide single crystals with hygroscopic nature[1].

Eu:Srl₂ single crystals with about 2 mm in diameter were grown by the μ-PD method. Transparent part were cut and polished for the optical characterization.
Grown crystals indicated a single phase of Srl₂ structure.

Emission 430 nm under X-ray irradiation was observed.
Light yield and energy resolution of Eu:SrI$_2$ crystals

**Pulse-height spectra**

- PMT (Hamamatsu, R7600U)
- $^{137}$Cs (662 keV)
- Eu:SrI$_2$ single crystals
- Eu10mol%
- Eu5mol%
- Eu7.5mol%
- Eu1mol%

**Eu concentration dependence of light yield and energy resolution**

<table>
<thead>
<tr>
<th>Eu Concentration (%)</th>
<th>Light Yield (ph/MeV)</th>
<th>Energy Resolution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu1%</td>
<td>~60,000</td>
<td>5</td>
</tr>
<tr>
<td>Eu5%</td>
<td>~65,000</td>
<td>4.6</td>
</tr>
<tr>
<td>Eu7.5%</td>
<td>~78,000</td>
<td>3.7</td>
</tr>
<tr>
<td>Eu10%</td>
<td>~60,000</td>
<td>4.4</td>
</tr>
</tbody>
</table>
Growth of 1 inch Eu:Srl₂ bulk crystal

During crystal growth

- Grown bulk crystals were cut and polished in the glove box and polished crystals were entered into the sealed container.
Growth of 1.5inch Eu:Srl$_2$ bulk crystal

1.5 inch Srl$_2$ as-grown crystal
Survey meter using Eu:Srl₂
What is the recent trend for the development of high performance scintillator?

1. Fine tuning of well-known materials
   i. Band gap engineering; GGAG, GSAG, ...

2. Higher technology for elaboration
   i. Hygroscopic materials
      LaBr₃, CLYC, SrI₂, Cs₃RECl₆, CsRE₂Cl₇, CsBa₂I₅: Eu, BaBrI:Eu, ...
   ii. Incongruent materials
      LPS, GPS, ..
   iii. Eutectic scintillator

3. Prospective
Ce:Lu$_2$Si$_2$O$_7$(LPS)


Ce:Gd$_2$Si$_2$O$_7$(GPS)

Ce:GPS
Gadolinium Pyro-Silicate
Ce:Gd$_2$Si$_2$O$_7$ (Ce:GPS)

Pulse height spectra
S. Kawamura+ 2008

Light output (photons/MeV)

Ce concentration

BGO
Ce2.5mol%:GPS

Ce:GSO

Counts

Light output (arb. unit.)

Pulse height spectra S. Kawamura+ 2008

R$_{Ce^{3+}}$ 1.14 A  R$_{La^{3+}}$ 1.16 A
La substitution in GPS

$$(\text{Ce}_{0.01}, \text{Gd}_{0.99-x}, \text{La}_x)_2\text{Si}_2\text{O}_7$$

La amount increase

X=0.05

La amount increase
Pulse height spectra (La-GPS)

Cs-137 irradiation
With PMT R7600-200

Escape peak

$\frac{\Delta E}{E}$ (FWHM)
4.4%@ 662 keV

RI source

sample

Photo multiplier
Hamamatsu
R7600-200

preAMP
ORTEC 113
C=1000pF

shaper
ORTEC 752A
Shaping time: 0.5µsec

MCA
8000A
Scintillation Decay Time

Excitation source Cs-137

Double Gaussian fit

<table>
<thead>
<tr>
<th>Primary</th>
<th>Secondary</th>
</tr>
</thead>
<tbody>
<tr>
<td>46 (79%)</td>
<td>346 (21%)</td>
</tr>
</tbody>
</table>

RI source

Photo multiplier
Hamamatsu
R7600-200

Oscilloscope
Tektronix
TDS 3034B
<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\Delta E/ E$ (%) @662keV (FWHM)</th>
<th>L.Y (photons/MeV)</th>
<th>Decay time (ns)</th>
<th>Density (g/cc)</th>
<th>Radiation length (cm) @511keV</th>
<th>Hygroscopicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaI :Tl</td>
<td>5.5</td>
<td>41,000</td>
<td>230</td>
<td>3.7</td>
<td>2.91</td>
<td>Yes</td>
</tr>
<tr>
<td>GSO:Ce (Gd$<em>{2}$SiO$</em>{5}$)</td>
<td>7.5</td>
<td>8,000</td>
<td>30-60</td>
<td>6.7</td>
<td>1.42</td>
<td>No</td>
</tr>
<tr>
<td>LYSO:Ce (LuYSiO$_{5}$)</td>
<td>6.7</td>
<td>32,000</td>
<td>48</td>
<td>7.1</td>
<td>1.12</td>
<td>No</td>
</tr>
<tr>
<td>LaBr$_{3}$:Ce</td>
<td>3.0</td>
<td>61,000</td>
<td>20-35</td>
<td>5.3</td>
<td>2.13</td>
<td>Yes</td>
</tr>
<tr>
<td>GAGG (Ce:Gd$<em>{3}$Ga$</em>{3}$Al$<em>{2}$O$</em>{12}$)</td>
<td>5</td>
<td>56,000</td>
<td>92</td>
<td>6.7</td>
<td>~1.7*</td>
<td>No</td>
</tr>
<tr>
<td>La-GPS</td>
<td>~5</td>
<td>~35,000</td>
<td>40-60</td>
<td>~5.5</td>
<td>~1.8*</td>
<td>No</td>
</tr>
</tbody>
</table>

Big bulk single crystal growth by Cz method
2inch La-GPS growth

Grown by C&A

2 inch

Cs-137 irradiation

Counts (a.u.)

MCA channel

Seed side

Tail side

<table>
<thead>
<tr>
<th>Serial Number</th>
<th>Energy resolution (662 keV, FWHM)[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>~ 7.0</td>
</tr>
<tr>
<td>#2</td>
<td>~ 6.2</td>
</tr>
<tr>
<td>#3</td>
<td>~ 8.3</td>
</tr>
<tr>
<td>#4</td>
<td>~ 9.8</td>
</tr>
</tbody>
</table>
Scintillator for oil logging

- Under ground ~6000m
- High temperature (over 150 °C)
- Good scintillation properties in high temperature

Ce: (La,Gd)$_2$Si$_2$O$_7$ (La-GPS)

La-GPS keeps high light yield and energy resolution even in 150°C

<table>
<thead>
<tr>
<th></th>
<th>Ce:La-GPS</th>
<th>Ce:GSO</th>
<th>Ti:Nal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density g/cm³</td>
<td>5.5</td>
<td>6.7</td>
<td>3.7</td>
</tr>
<tr>
<td>λ : nm</td>
<td>390</td>
<td>430</td>
<td>420</td>
</tr>
<tr>
<td>L.Y@150°C ph/MeV</td>
<td>40,000</td>
<td>10,000</td>
<td>13,000</td>
</tr>
<tr>
<td>E.R.@150°C %@662keV</td>
<td>~9</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>decay time : ns</td>
<td>46</td>
<td>30-60</td>
<td>250</td>
</tr>
<tr>
<td>Self radiation</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>
What is the recent trend for the development of high performance scintillator?

1. Fine tuning of well-known materials
   i. Band gap engineering; GGAG, GSAG, ...

2. Higher technology for elaboration
   i. Hygroscopic materials
      LaBr$_3$, CLYC, SrI$_2$, Cs$_3$RECl$_6$, CsRE$_2$Cl$_7$, CsBa$_2$I$_5$: Eu, BaBrI:Eu, ...
   ii. Incongruent materials
       LPS, GPS, ..
   iii. Eutectic scintillator

3. Prospective
Digital radiography

Vapour deposited column-shaped CsI:Tl.
Diameter $\sim 3 \, \mu m$, length $> 0.5 \, mm$. 
Characteristics of Eutectic Scintillator Crystals

Present scintillators

Gd$_2$O$_2$S(GOS) array

Tl:CsI needle scintillator

Spatial resolution of devices using present scintillators is not sufficient.

Eutectic scintillators

Phase-separated structure

Fiber-like (GdAlO$_3$/Al$_2$O$_3$)


High-resolution (total reflection by light guide)

Ref.[2]: N. Yasui et al., Advanced Materials 2012
GdAlO$_3$-Al$_2$O$_3$ Eutectic Crystal by the $\mu$-PD method

FIG. 1. Structure of the GdAlO$_3$(GAP):Ce$^{3+}$-Al$_2$O$_3$ phase-separated scintillator fibers (PSSFs). (a) Schematic view of the GAP:Ce$^{3+}$-Al$_2$O$_3$ PSSFs. (b) Diagonal view of the cut and polished sample ($2.3 \times 2.3 \text{ mm} \times 1100 \mu\text{m}$). (c) SEM image of the sample edge. (d) Enlarged SEM image of the dashed square in (c).
Eu doped LiF/LiBaF$_3$/CaF$_2$

LiF (Cubic, $n=1.39$ [$^{[1]}$])
CaF$_2$ (Cubic, $n=1.44$ [$^{[2]}$])
LiBaF$_3$ (Cubic, $n=1.54$ [$^{[1]}$])

Volume ratio
(LiF : CaF$_2$ : LiBaF$_3$ = 33.7 : 26.3 : 40.0)

Eutectics fabricated at the composition were composed of three phases.

LiF/LiBaF$_3$/CaF$_2$

Rod phases were well dispersed.
Fiber-like structure was well constructed.

Material with light guide property was obtained!!
Eu doped LiF/LiBaF$_3$/CaF$_2$

Fig. 30. Radio-luminescence spectra under $\alpha$-ray excitation $^{241}$Am radiation source

Fig. 31. Pulse-height spectra of the eutectic under neutron excitation from $^{252}$Cf radiation source with PMT (Hamamatsu R7600U-200).

Advantages
- High Li concentration (Li: 0.045 mol/cm$^3$, LiCaAlF$_6$: 0.016 mol/cm$^3$)
- Low density 3.8 g/cm$^3$
- Non hygroscopic
- Good light yield (7000 photons/neutron)
- Fiber-like structure
- Scintillation in rod phases
- Light guide property

Scintillation in rod phases and light guide property was obtained. This eutectic showed good light yield.
Important parameters for gamma-ray scintillator

- high light output
- scintillation speed
- good energy resolution
- high $Z_{\text{eff}}$
- high density
- large size of crystal
- low cost per cm$^3$
- low afterglow
- low intrinsic activity
- High radiation hardness

$Y$ (photons/MeV)
$\tau_s$ (ns)
$R_{\text{FWHM}}$ (%)
$\rho$ (g/cm$^3$)
10-100 cm$^3$
Prospective

1. Fine tuning of well-known materials
   i. Band gap engineering; GGAG, Pr:LuAG

2. Higher technology for elaboration
   i. Hygroscopic materials
      LaBr$_3$, CLYC, SrI$_2$, Cs$_3$RECl$_6$, CsRE$_2$Cl$_7$, CsBa$_2$I$_5$: Eu, BaBrI:Eu, ...
   ii. Incongruent materials
       LPS, GPS, ..
   iii. Eutectic scintillator
       Bulk crystal growth
<table>
<thead>
<tr>
<th></th>
<th>Mg-co-doped\nGAGG</th>
<th>GAGG</th>
<th>Ce:GAGG-Ga2.4</th>
<th>La-GPS</th>
<th>Srl₂</th>
<th>Pr:LuAG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density g/cm³</td>
<td>6.67</td>
<td>6.67</td>
<td>6.51</td>
<td>5.5</td>
<td>5.46</td>
<td>6.7</td>
</tr>
<tr>
<td>Decay time ns</td>
<td>~40</td>
<td>90</td>
<td>138</td>
<td>40-80</td>
<td>1200-1400</td>
<td>20</td>
</tr>
<tr>
<td>Hygroscopicity</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>L.Y. photon/MeV</td>
<td>45000</td>
<td>57000</td>
<td>45000</td>
<td>37000</td>
<td>~80000</td>
<td>20000</td>
</tr>
<tr>
<td>E.R. %@662keV</td>
<td>5.5</td>
<td>5.2</td>
<td>3.8</td>
<td>5-6</td>
<td>3-4</td>
<td>4.8</td>
</tr>
<tr>
<td>m.p., °C</td>
<td>1900</td>
<td>1900</td>
<td>1900</td>
<td>1900</td>
<td>538</td>
<td>2050</td>
</tr>
<tr>
<td>λ em nm</td>
<td>520</td>
<td>520</td>
<td>516</td>
<td>390</td>
<td>435</td>
<td>310</td>
</tr>
<tr>
<td>Self radiation</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>La</td>
<td>no</td>
<td>Lu</td>
</tr>
</tbody>
</table>
# 株式会社C&A 会社概要

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>設立年月日</td>
<td>平成24年11月7日</td>
<td></td>
</tr>
<tr>
<td>企業理念</td>
<td>材料10年説を覆す！大学発材料・デバイスを迅速に製品化！</td>
<td></td>
</tr>
<tr>
<td>所在地</td>
<td>〒980-8579 仙台市青葉区荒巻字青葉6-6-40 T-Biz(東北大学連携ビジネスインキュベータ)</td>
<td></td>
</tr>
<tr>
<td>代表者</td>
<td>代表取締役社長 鎌田圭(前 古河機械金属㈱ シンチレータ結晶Gr.リーダー) 代表取締役CTO 東北大学金属材料研究所 教授 吉川彰</td>
<td></td>
</tr>
<tr>
<td>事業内容</td>
<td>結晶材料の製造販売、特性評価、デバイス試作・販売、コンサルティング</td>
<td></td>
</tr>
<tr>
<td>主な取引先</td>
<td>海外：NASA、ハーバード大、チェコ物理研、FOMOS、 国内：TDK、東芝ITC、千代田テクノル、東大、浜松ホトニクス、</td>
<td></td>
</tr>
<tr>
<td>備考</td>
<td>資本金：550万円</td>
<td></td>
</tr>
</tbody>
</table>

シンチレータ単結晶とデバイス

| Ce:GAGG | Pr:LuAG | アレイ化、デバイス化 | LTGA | CTGS | 各種圧電デバイス |

圧電単結晶とデバイス
シンチレータ結晶

GAGG
Eu:SrI₂
La-Gd₂Si₂O₇

圧電結晶・デバイス

CTGAS

結晶作製装置
Thank you for your attention!

This work was partially supported by following projects and cooperation:

- Czech MSMT projects ME953 and 1M06002.
- Furukawa Co.Ltd.
- Tokuyama Co. Ltd.
- Konoshima Chemical Co. Ltd.
- Sendai Medical Imaging Clinic