Scintillation phenomenon in solids: History, principles, characteristics and practical applications

Martin Nikl
Institute of Physics, AS CR, Prague, Czech Republic
Internet search for the word “scintillator” provides 52,600 sites using Yahoo search engine …

…..but what is it good for ???
• Principle
• Something from their history
• Technology of preparation
• Underlying physics
• Parameters, characteristics and methods
• Applications
• An example of concerted research at aluminum garnets
• Suggested literature
**Principle of a scintillator**

1 photon (keV - GeV)  

n photons (2 - 4 eV)

Counting of HE photons!  
Fast response needed!

Why we need it … above few keV there are no efficient direct-conversion detection elements (photon-to-electrical pulse)
Scintillation detector = scintillator+photodetector
⇒ registration of X-rays or γ-radiation, energetic particles or ions.

Scintillator TRANSFORMS high-energy photons into photons in UV/VIS spectral region, which one can easy and with high sensitivity register by the conventional detectors.

PD, APD, CMOS, CCD …
Si, GaAs, GaN, InGaN, SiC, diamond
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.

CaWO$_4$ powder in 1986

---

**Year of introduction of a scintillation material**

- 1940: CaWO$_4$
- 1960: Bulk single crystals (e.g., CsI:TI, NaI:TI)
- 1980: Y$_3$Al$_5$O$_{12}$:Ce, Lu$_3$Al$_5$O$_{12}$:Pr
- 2000: Lu$_2$SiO$_5$:Ce, PbWO$_4$, CeF$_3$ (X=Cl,Br)
Czochralski technology

- Chamber
- Carbon heater
- Carbon
- Pt crucible
- Computer control
- Rotary pump
- Diffusion pump

Yoshikawa Lab, IMRAM, Tohoku university, Sendai, Japan

8 inch-size BaF₂

Czochralski grown PbWO₄
IP Prague, CR

Czochralski grown YAlO₃:Ce, Lu₃Al₅O₁₂:Ce,
CRYTUR LtD. Turnov, CR
Micro-pulling-down technology

Yoshikawa Lab, IMRAM, Tohoku university, Sendai, Japan

Grown crystals

Undoped YAP
Pr 0.1 mol%
Pr 0.5 mol%

BaF₂ crystal
Other solid state systems&technologies

LPE-grown single crystalline films, Y(Lu)AG:Ce,

SrHfO$_3$:Pb microcrystalline phosphor

Ce-doped silica glass sol-gel technology (to make scint.fibers Veronese Fr-1)

Vapour deposited column-shaped CsI:Tl Diameter ~ 3 µm, length > 0.5 mm.

YAG-based optical ceramics
Physics of scintillators

**CONVERSION** - interaction of a high-energy photon with a material through photoeffect, Compton effect, pair production, appearance of electron-hole pairs and their thermalization

**TRANSPORT** - diffusion of electron-hole pairs (excitons) through the material, possible (repeated) trapping at defects, nonradiative recombination

**LUMINESCENCE** - trapping of charge carriers at the luminescence centre and their radiative recombination
Parameters, characteristics, and methods

- Integral scintillation efficiency
- Photoelectron (Light) yield and Energy resolution
- Emission wavelength
- Speed of scintillation response
- Density ($Z_{\text{eff}}$)
- Radiation resistance
- Chemical composition
- Price

Material with all the top parameters doesn’t exist so that there is always a search for tailored materials for particular applications where only one or more parameters are recognized as the critical ones.
Integral scintillation efficiency

Absolute comparison of radioluminescence spectra of a material with the standard sample in the same experimental conditions

Integral efficiency $\eta = \beta \cdot S \cdot Q$ equals to multiplied sub-efficiencies of the conversion, transport and luminescence stages
**Photoelectron (Light) yield**

Photoelectron yield of YAP:Ce

Excitation - 662keV photons (\(^{137}\)Cs)

**Light yield** measurement consists in the measurement of the charge collected at the photomultiplier anode within certain time gate (typ. 1 \(\mu\)s), i.e. \(U.I.\Delta t\), after the absorption of high energy photon. Result of measurement is scaled within multichannel analyzer memory (pulse height analysis mode) and repeated many times to get reasonable statistics and well-resolved photopeak (obtained only if complete absorption of HE photon can be obtained in the sample, i.e. sufficiently big sample is needed).

**Energy resolution** is defined from the FWHM of the photopeak. (typical values are 5-15% at 662 keV)

**Photoelectron yield** divided by quantum efficiency of photocathode provides **Light yield - given in [photons/MeV]** the best classical materials as NaI:Tl,CsI:Tl give 40 000-50 000 phot/MeV , BGO gives 8 000 phot/MeV.
Photoelectron (light) yield nonproportionality

The non-proportionality of the $N_{\text{phels}}(E)$ photoelectron yield of LuAG:Pr Cz-grown crystal normalized to $N_{\text{phels}}$ yield of $^{137}\text{Cs}$ 662 keV energy line.

Photoelectron yield value (per MeV) depends on the energy of the incoming HE photons!!

Conversion of high energy photon into many electron-hole pairs at the end of Conversion stage is many-step process with non-unique pathway. Elementary steps are differing in “production yield” of final e-h pairs, closely spaced excitations may interact, material defects make it even more complex, etc.

See also Vasil’ev Mo-3, Moszynski Tu-13.
Position of the emission spectrum is important for the choice of the photodetector. In the case (a) PMT with quartz window (more expensive) is needed, (b) is an optimum position for a standard S20-photocathode PMT, (c) is better suited for a photodiode (or CCD) detector.

Today, however, there is tremendous development of UV-sensitive semiconductor photodetectors based on SiC, GaAlN and diamond!
Optical coupling between scintillator and photodetector

By far not all the UV/visible light generated in scintillator can be delivered to the photodetector due to self-absorption, internal reflection, scattering losses, etc.

Si mold

Patterned polymer

GaN diode struct

Photonic bandgap on the surface for better light extraction!!
Speed of scintillation response

1 photon (keV - GeV)  n photons (1 - 6 eV)

\[ I(t) = \sum A_i \exp\left[-\frac{t}{\tau_i}\right] \]

Duration of the output light pulse is determined by the luminescence decay time of the emission centers, but also by the timing characteristics of the transport stage.
Examples of scintillation decay

**LuAG:Ce0.12%**
- **60-70 ns**
- **54 ns**
- **600-900 ns**

\[ \alpha = \frac{I_s}{I_{tot}} \times 100\% \]

**LYSO:Ce Photonics**
- **decay time: 45 ns**

“Background increase” due to slow decay components in scint. decay

In Ce-doped scintillators the shallow electron traps are responsible for slower scintillation components
Trapping-detrapping Processes

Ionizing radiation

(X, γ...)

Radio luminescence

A – direct process

B – delayed process

Studied by TSL and TSC experiments (lectures in next days)
Radiation damage (resistance)

Absorption spectra of YAP:Ce before ($A_0$) and after ($A_{irr}$) X-ray irradiation (dose 500 Gy)

Induced absorption spectrum $\mu(\lambda)$
YAP:Ce, D=500 Gy, RT

$$\mu(\lambda) = 2.3 \times (1/l) \times (A_{irr}(\lambda) - A_0(\lambda))$$

Induced absorption is caused by the relocation of charge carriers into the deep traps (can be monitored by TSL measurement above RT). Occupied deep traps introduce the additional=induced absorption bands (color centers).

In the case of YAP:Ce such traps can be partly suppressed by tetravalent Zr$^{4+}$ ion doping.
Parameters of selected scintillation materials

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LY Pho/MeV Fast/slow</td>
<td>4-5x10^4</td>
<td>6.3x10^4</td>
<td>1-3x10^2</td>
<td>~2x10^4</td>
<td>1.5-1.9x10^4</td>
<td>8x10^3</td>
<td>2.7-3.2x10^4</td>
</tr>
<tr>
<td>Decay tm [ns] Fast/slow</td>
<td>--/1000</td>
<td>16/ --</td>
<td>2+10/ 100-10^4</td>
<td>20-38/ 100-10^4</td>
<td>55-65/ 500-10^3</td>
<td>~/300</td>
<td>40/-</td>
</tr>
<tr>
<td>Density g/cm^3</td>
<td>4.51</td>
<td>5.08</td>
<td>8.23</td>
<td>5.36</td>
<td>6.67</td>
<td>7.13</td>
<td>7.41</td>
</tr>
<tr>
<td>Chem. Compos.</td>
<td>CsI:Tl</td>
<td>LaBr_3:Ce</td>
<td>PbWO_4</td>
<td>YAlO_3:Ce</td>
<td>Lu_3Al_5O_{12}:Ce</td>
<td>Bi_4Ge_3O_{12}</td>
<td>Lu_2SiO_5:Ce</td>
</tr>
</tbody>
</table>
Applications of scintillators

**Medical application**
- PET, SPECT, CT

**High energy physics**
- Particle physics, ...

**Security check**
- X-ray scanning

**Nondestructive analysis**
- Computed tomography

**X&Neutron-based**
- Remote detection

**Other applications**
- Checking point
- Radon detection, geology
Collinearly emitted annihilation quanta detected in coincidence

Detector ring (inner diam. ~ 0.8 m)

Detectors BGO + PM

Positron Emission Tomography

Radiopharmaceutical

Coming Lu(Gd)$_2$SiO$_5$:Ce

TOF, DOI modifications under development

Radiation in Medicine **Diagnostics** Radioisotope imaging
PET systems
Siemens-CTI

http://www.epub.org.br/cm/n01/pet/pet_hist.htm
Simultaneous PET and MR imaging

**FIGURE 11.1.** Interactive image registration of an FDG-PET study to a $T_1$-weighted MR study of the same patient by using the PMOD image fusion tool (www.pmod.com). Images of orthogonal slices through the MRI and the PET data sets are shown in the first row and the second row, respectively. The third row shows a fusion of the studies with the current coordinate transformation by using image blending and a contour overlay.
Typical X-irradiation dose in a CT scan is 20x higher than that of simple lung check … should be used with caution!
CT – „whole body“ spiral scan

my knees
Security check … by far not only luggages!

- About 200 millions of containers travel every year, and only about 1 to 2 % of them are directly controlled !!!
- Check for drugs, explosives, radioactive material at seaports and airports  HOMELAND SECURITY!!!
Remote detection

- multiple irradiation sources (X-ray, neutrons)
- sensitive not only to material density, but also to its elemental composition (explosives)
- on-line evaluation of moving goods
- mobile stations with short installation times
- easy to handle and use

- high light yield and mechanically/chemically stable scintillator for X-ray detection
- tuned-composition (Li-B-Gd containing) material for neutron detection
Compact Muon Solenoid detector in Large Hadron Collider in CERN, Geneva

PbWO$_4$-based calorimetric detector

search for Higg’s boson …..

about 80,000 single crystal blocks of about 3x3x22 cm (12 m$^3$) produced in Russia and China, LHC launch expected 10/2009!
High resolution 2D-imaging experiment under X-ray (accelerated electrons)

Sub-µm resolution needed!
Better 2D-resolution requires thinner scintillator layer!

Made by CRYTUR Ltd, CR
Scintillator screens, experimental set-up

LPE-grown LuAG:Ce-on-YAG films and single crystal plate on substrate

Whole LPE film on one side and 5 µm on the other side were polished away

Experimental set-up for 2D imaging
Overview of the scintillator screens used

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sample type</th>
<th>Film/plate material</th>
<th>Film/plate [µm]</th>
<th>Substrate [mm]</th>
<th>Scintil. eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lu-6</td>
<td>LPE SCF</td>
<td>LuAG:Ce</td>
<td>17</td>
<td>0.5</td>
<td>70</td>
</tr>
<tr>
<td>Lu-9</td>
<td>LPE SCF</td>
<td>LuAG:Ce</td>
<td>29</td>
<td>0.5</td>
<td>67</td>
</tr>
<tr>
<td>Lu-11</td>
<td>LPE SCF</td>
<td>Lu$<em>{0.8}$Y$</em>{0.2}$AG:Ce</td>
<td>15</td>
<td>0.5</td>
<td>61</td>
</tr>
<tr>
<td>Lu-16</td>
<td>LPE SCF</td>
<td>Lu$<em>{0.6}$Y$</em>{0.4}$AG:Ce</td>
<td>27</td>
<td>0.5</td>
<td>62</td>
</tr>
<tr>
<td>Cz-2</td>
<td>Bulk Cz</td>
<td>LuAG:Ce</td>
<td>20</td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>Cz-3</td>
<td>Bulk Cz</td>
<td>LuAG:Ce</td>
<td>20</td>
<td>3</td>
<td>92</td>
</tr>
</tbody>
</table>
2D imaging capability of LPE films and SC plates

The grid image obtained by Lu-6 sample screen (upper left) with the detail of wire crossing (lower left) and the same picture obtained by Cz-3 sample screen (right)
Some more images by SC LuAG: Ce plate sensor

A tick

Aluminum structure

A circuit from calculator

Coaxial cable with BNC connector
Strategy for scintillator materials research

Correlation of several techniques at specifically prepared sample set under well-defined technological conditions:

- **Time-resolved emission spectroscopy** – to interconnect the luminescence (scintillation) kinetics with the occurrence or non of the defects visualized by the above techniques

- **Specific experiments** for determination of scintillation characteristics (Phel. yield, scintillation decay, radiation damage)

- **Thermoluminescence** – to visualize trapping states, which take part in the radiative processes, spectra can advise on recombination sites

- **Thermally stimulated currents** – to visualize complementary nonradiative processes

- **Electron paramagnetic (spin) resonance** – to understand location of unpaired-spin-containing trapping centers
Integral eff. & LY in Ce$^{3+}$-doped Y$_3$Al$_5$O$_{12}$ and Lu$_3$Al$_5$O$_{12}$

X-ray excited luminescence

![Graph showing X-ray excited luminescence with intensity and wavelength axes.]

- **YAG:Ce0.32%**
- **LuAG:Ce0.12%**
- **BGO x5**

**Light yield (1 µs time gate)**

- Best YAG:Ce $\sim 3x$ BGO
- Best LuAG:Ce $\sim 60\%$ of YAG:Ce

**A lot of “slow light” in these materials**

![Graph showing scintillation decay with time and intensity axes.]

- LuAG:Ce
  - Scintillation decay pulsed x-ray, em = 500 nm
  - 58 ns (30%)
  - 150 ns + 600 ns (70%)

Retrapping of electrons at shallow traps before their radiative recombination at Ce$^{3+}$ ions

Nikl et al, pss (a) 201, R41 (2004)
Ce-doped YAG and LuAG

A number of the electron traps indicated by TSL glow curve below RT delays electron delivery to Ce$^{4+}$ and slows down the scintillation response.

“Background increase” due to slow decay components in scint. decay.

YAG:Ce0.32%

LuAG:Ce0.12%

TSL after X-ray irr. at 10 K
Antisite defects in YAG and LuAG single crystals

Exchange of Y(Lu) and Al ions is an inevitable consequence of the growth from high temperature melt.
Comparison of YAG:Ce single crystal and optical ceramics


TSL peak at 92 K is due to liberation of electron from the antisite $Y_{Al}$ defect trap and recombination with Ce$^{4+}$ hole center.

Sintering temperature of ceramics is about 1700 °C applied for several hours, while SC growths from the melt close to 1970 °C

TSL peak at 92 K is the dominant feature in all YAG:Ce single crystals studied
Electron traps related to the antisite Lu$_{\text{Al}}$ defects in LuAG:Ce

Triple peak structure at 142 K, 167 K and 190 K is always dominant in single crystals, while it is completely absent in Liquid Phase Epitaxy-grown layers.

TSL spectra within these peaks contain only Ce$^{3+}$ emission

Liberation of electrons from the antisite-defect-related trap and their recombination with Ce$^{4+}$ is proposed to explain TSL characteristics in this temperature region

As the energy depth of AD-related trap is higher with respect to YAG:Ce, it explains more detrimental influence on scintillation decay and LY characteristics !!

Δ$E =$ 0.29 eV 0.40 eV 0.47 eV

Nikl et al, phys.stat.sol. (b) 242, R119 (2005)
Antisite defects in Al garnets

High-resolution spectroscopy of the Nd$^{3+}$ satellite emission lines in YAG:Nd

XRD from an increase of lattice constant in YGG:Yb single crystal and ceramics
Shirinyan et al, NIM A 537 (2005)

Newly by EPR evidenced Ce$^{3+}_{\text{Al}}$ and Ce$^{3+}$ perturbed by Lu$_{\text{Al}}$ centers!
Laguta et al, LUMDETR 2006, Lviv

Ce$^{3+}$ at Lu site perturbed by the Lu$_{\text{Al}}$ antisite defect
⇒ Ce and Lu$_{\text{Al}}$ defect might be spatially correlated!!
TSL dependence on the Ce concentration in LuAG:Ce – region 1 and 2

Diminishing of “undoped-related” TSL features within 50-80 K with increasing Ce concentration

Competition between TSL signals within 50-120 K and 120-200 K!

After X-ray irradiation at any $T \in (10-100) \text{ K}$ phosphorescence decay doesn’t depend on temperature and follows $t^{-1}$ law

Tunneling process between the trapped electron and hole counterparts (spatially correlated)
Scintillation decay of LuAG:Ce at RT

The exponential and power function components account for the first and second stage of the scintillation decay, respectively.

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.

Instead, coefficient alpha and amplitude of the 140 K TSL peak seem to be correlated and related to the time development of recombination processes at similar time scales.
Radiative recombination process in LuAG:Ce (Pr)

At RT, $\tau > 30\ \mu$s

Above 50 K there is possibly already thermally assisted tunnelling process (slight T dependence of p)

---

CB

$\sim t^{-1}$

VB

Ce$^{3+}$

AD-related electron trap

(Pr$^{3+}$)
Admixture of Ga to suppress AD-related trapping phenomena in LuAG:Pr (Ce)

Energy transfer and storage in LuAG:Ce(Pr) SC

- Electron traps associated with Lu$_{\text{Al}}$ antisite defects were evidenced in LuAG host. TSL triple peak at 142 K, 167 K and 190 K (region 2) is due to electron libration from Lu$_{\text{Al}}$ trap and its recombination with the Ce$^{4+}$ (Pr$^{4+}$) hole center. In YAG host an analogous situation holds for 92 K TSL peak.

- EPR evidences a possibility of spatial correlation of Ce$^{3+}$ and Lu$_{\text{Al}}$ defect, which is reflected in the existence of tunneling process observed in TSL glow curves (region 1) supported by the $t^{-1}$ course of low temperature phosphorescence decay.

- TSL process thus indicates the existence of both thermally activated “above-the-gap” (region 2) and “sub-gap tunneling” (region 1) recombination processes between an AD-trapped electron and Ce$^{4+}$ (Pr$^{4+}$) hole center, where the latter process is responsible for the observed slower component in the scintillation decay.

- Ga-admixture considerably diminished the AD-trap related phenomena: host luminescence suppressed, TSL peaks washed out, scintillation decay accelerated. However, it seems that Lu$_{\text{Al}}$ defects could be “burried” in the lowered bottom of CB rather than simply suppressed due to the Ga occupation of the Al octahedral site. Somewhat lowered LY and form of the Pr$^{3+}$ excitation spectra within 170-200 nm might indicate an additional nonradiative loss channel induced by the Ga doping.
Perspectives

- Sources of energetic radiation and particles are more and more used in different fields of human activity ⇒ increasing need for tailored scintillation materials

- Difficult to “invent” competitive completely new materials as in some parameters we are close to intrinsic limits, but new technologies (ceramics) can bring unexpected solutions

- Lack of the detailed understanding the physical mechanisms in existing materials ⇒ room for their optimization (recent example of PbWO₄)

- Driving forces for scintillator development will come from medical and high-tech industrial applications, homeland security, space technology
Suggested literature