# 2. Scintillation and luminescent materials. History. Application and Technological challenges

## 2.1. Definition of the scintillation and luminescent materials

The origin and meaning of the terminology related to scintillators and luminescent materials must first be explained.

The word **luminescence** was first used by Eilhardt Wiedemann, a German physicist, in 1888, it refers to the emission of light by a substance not resulting from heat.This word originates from the Latin word *lumen*, which means light. Presently, the word *luminescence* is defined as a phenomenon in which the electronic state of a substance is excited by some kind of external energy and the excitation energy is given off as light. Here, the word *light* includes not only electromagnetic waves in the visible region of 400 to 700 nm, but also those in the neighboring regions on both ends, i.e., the near-ultraviolet and the near-infrared regions.

There are several varieties of luminescence, each named according to the source of exciting energy, or the trigger for the luminescence:

- **Photoluminescence** is luminescence where the energy is supplied by electromagnetic radiation. In modern usage, light emission from a substance during the time when it is exposed to exciting radiation is called *fluorescence*, while the after-glow if detectable by the human eye after the cessation of excitation is called *phosphorescence.*
- **Chemiluminescence** is luminescence where the energy is supplied by chemical reactions.
- **Triboluminescence** is phosphorescence that is triggered by mechanical action or electroluminescence excited by electricity generated by mechanical action. Some minerals glow when hit or scratched.
- **Electroluminescence** is luminescence caused by electric current.
- **Cathodoluminescence** is electroluminescence caused by electron beams; this is how television pictures are formed on a CRT (Cathode Ray Tube).
- **Radioluminescence** is luminescence caused by ionising radiation, such as $\alpha$-, $\beta$-, gamma rays, X-rays.

The definition of the word ***phosphor*** itself is not clearly defined and is dependent on the user. In a broad sense, the word phosphor is equivalent to "solid luminescent material."

**Luminescent Materials** such as phosphors are materials that emit light (infrared to ultraviolet) under external energy excitation. The incident energy, in the form of high energy electron, photons, or electric field, can then be re-emitted in the form of electromagnetic radiation.

**Scintillators** are materials that absorb high energetic radiation, such as $\alpha$-, $\beta$-, gamma rays, X-rays, neutrons or high energetic particles, and convert that energy into bursts of visible photons. These photons are then converted into electrical pulses by photo-detectors.

| | | |
|---|---|---|
|  |  |  |
| **Inorganic Crystal Scintillators** | **Pastic Scintillators** | **Organic Liquid Scintillators** |

Scintillation materials exist in many physical forms, including:

- **Organic Crystal Scintillators** – Organic crystal scintillators are aromatic hydrocarbon compounds which contain benzene ring structures interlinked in various ways. Their luminescence typically decays within a few nanoseconds. They are very durable, but their response is anisotropic (which spoils energy resolution when the source is not collimated), and they cannot be easily machined, nor can they be grown in large sizes; hence they are not very often used.
- **Organic Liquid Scintillators** – Organic liquid scintillators are liquid solutions of one or more organic scintillators in an organic solvent. The typical solutes are fluors and wavelength shifter scintillators. For many liquids, dissolved oxygen can act as a quenching agent and lead to reduced light output, hence the necessity to seal the solution in an oxygen-free, air-tight enclosure.
- **Plastic Scintillators** – The term plastic scintillator typically refers to a scintillating material in which the primary fluorescent emitter, is suspended in a solid polymer matrix. The advantages of plastic scintillators include fairly high light output and a relatively quick signal, with a decay time between 2-4 nanoseconds, but perhaps the biggest advantage of plastic scintillators is their ability to be shaped, through the use of molds or other means, into almost any desired form with what is often a high degree of durability.
- **Inorganic Crystal Scintillators** –are usually crystals often with a small amount of activator impurity. Inorganic crystals have superior performance for the detection of high-energy gamma rays.
- **Gaseous Scintillators** – Gaseous scintillators consist of nitrogen and the noble gases helium, argon, krypton, and xenon, with helium and xenon receiving the most attention. The scintillation process is due to the de-excitation of single atoms excited by the passage of an incoming particle.
- **Glass Scintillators** – Glass scintillators are sensitive to electrons and $\gamma$ rays as well (pulse height discrimination can be used for particle identification). Being very robust, they are also well-suited to harsh environmental conditions. Glasses and glass fibers are often used for neutron detection.

- **Ceramic Scintillators** are commonly used for X-ray imaging, and nanophase-powders allow the synthesis of special compositions that, if successfully developed, may become improved alternatives to single crystal scintillators.

Scintillators are useful for sensing alpha, beta and gamma radiation as well as other nuclear particles and in some cases determining the particle type. For example, organic scintillators can sense fast neutrons emitted spontaneously from fissile isotopes of uranium and plutonium, enabling passive detection of nuclear weapons. The detection and identification of subatomic particles is not only important for nuclear non-proliferation efforts but is a wide-ranging scientific problem with implications for medical devices, radiography, biochemical analysis, particle physics, and even astrophysics (see also the paragraph 2.3 for more information).

The key element of all radiation instruments is radiation detector. A scintillation detector or scintillation counter is obtained when a scintillator is coupled to an electronic light sensor such as a photomultiplier tube (PMT) or a photodiode. PMTs absorb the light emitted by the scintillator and reemit it in the form of electrons via the photoelectric effect. The subsequent multiplication of those electrons (sometimes called photo-electrons) results in an electrical pulse which can then be analyzed and yield meaningful information about the particle that originally struck the scintillator. Solid-state crystal detectors are practically the only type of sensors that can ensure both detection of the invisible radiations and determination of their type and radiation spectrum. Combination of high efficiency of radiation detection, high sensitivity, and possibility to determine the energy characteristics have made scintillation detectors one of the main types of sensors used in instruments and systems for detection and monitoring of ionizing radiation.

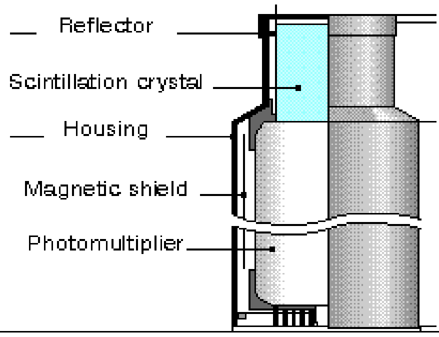



**Table 1:Scintillation detectors on the base of NaI:Tl, CsI:Tl, CsI:Na, CsI:$CO_3$ , CsI pure, LiI:Eu crystals (ISMA sources) example)**

### Basic principles of radiation detection

Radiation, such as X-ray etc. has high penetrating power and this property is useful in various fields. Scintillators convert it into visible light which then can be easily transformed to electrical signal by photomultiplier or avalanche photodiode. Finally, information including an imaging, a spectrum, and timing is processed by computer.

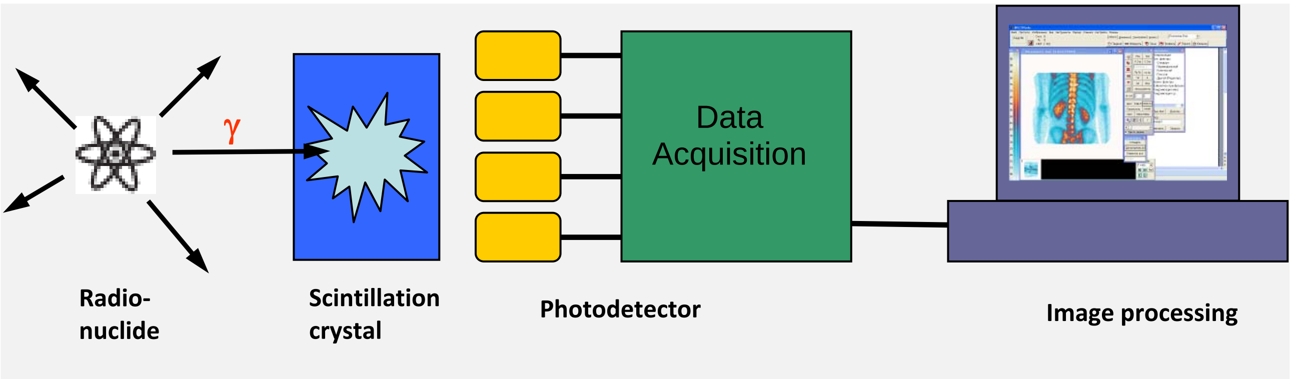



Table 2: radiation detection principle

**Scintillation and luminescent materials research and development** is located on the cross-roads of some scientific branches: chemistry, material science, physics of solids, crystal growth and the physics of films, luminescence and optics, scintillation physics and radiation detection detectors engineering, signal detection technologies and many other science fragments. Each of these sciences has its own characteristics and its landscape.

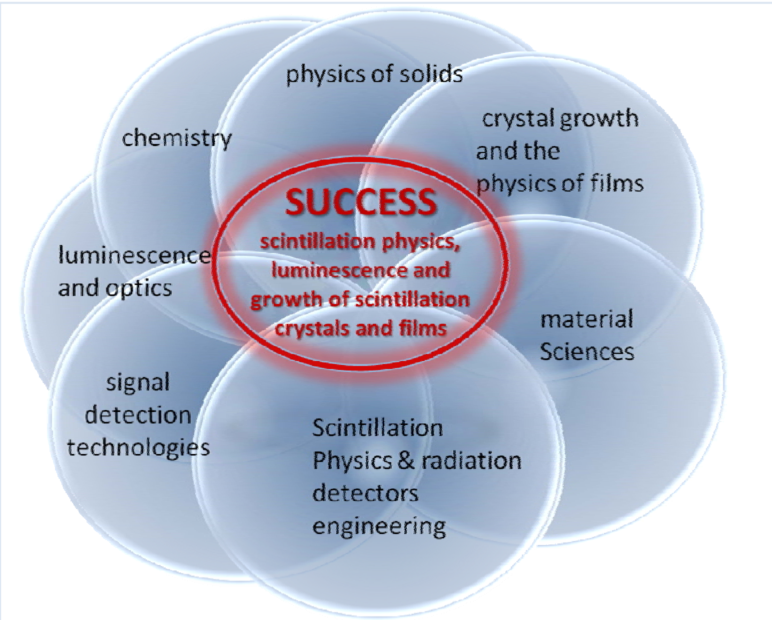



Table 3 :SUCCESS project's technical focus

The same is true with respect to crystal growth. According to their types and growth methods, the science of crystal growth can be divided into a great number of science fragments: silicon, semiconductors, bio-objects, three-dimensional crystals and films (epitaxial growth), growth from melt and solution, etc...

**The purpose of the SUCCESS project lies in the area of scintillation physics, luminescence and growth of scintillation crystals and films.**

However, it is to be highlighted that SUCCESSS project purpose essentially concerns the R&D aspect in the field of luminescence and marginally in the crystal growth.

**Thus, the scientific, applied and market landscapes in SUCCES case are very specific as formed from the landscapes of a great number of other sciences.**

## 2.2. Short history of scintillators and luminescent materials science

The use of scintillation to detect radiation is a century old. A history of the discovery of important inorganic scintillator materials—important in the sense that they either became commercially available and widely used or triggered further developments or new research directions. The discovery of scintillator materials may be divided into three phases.

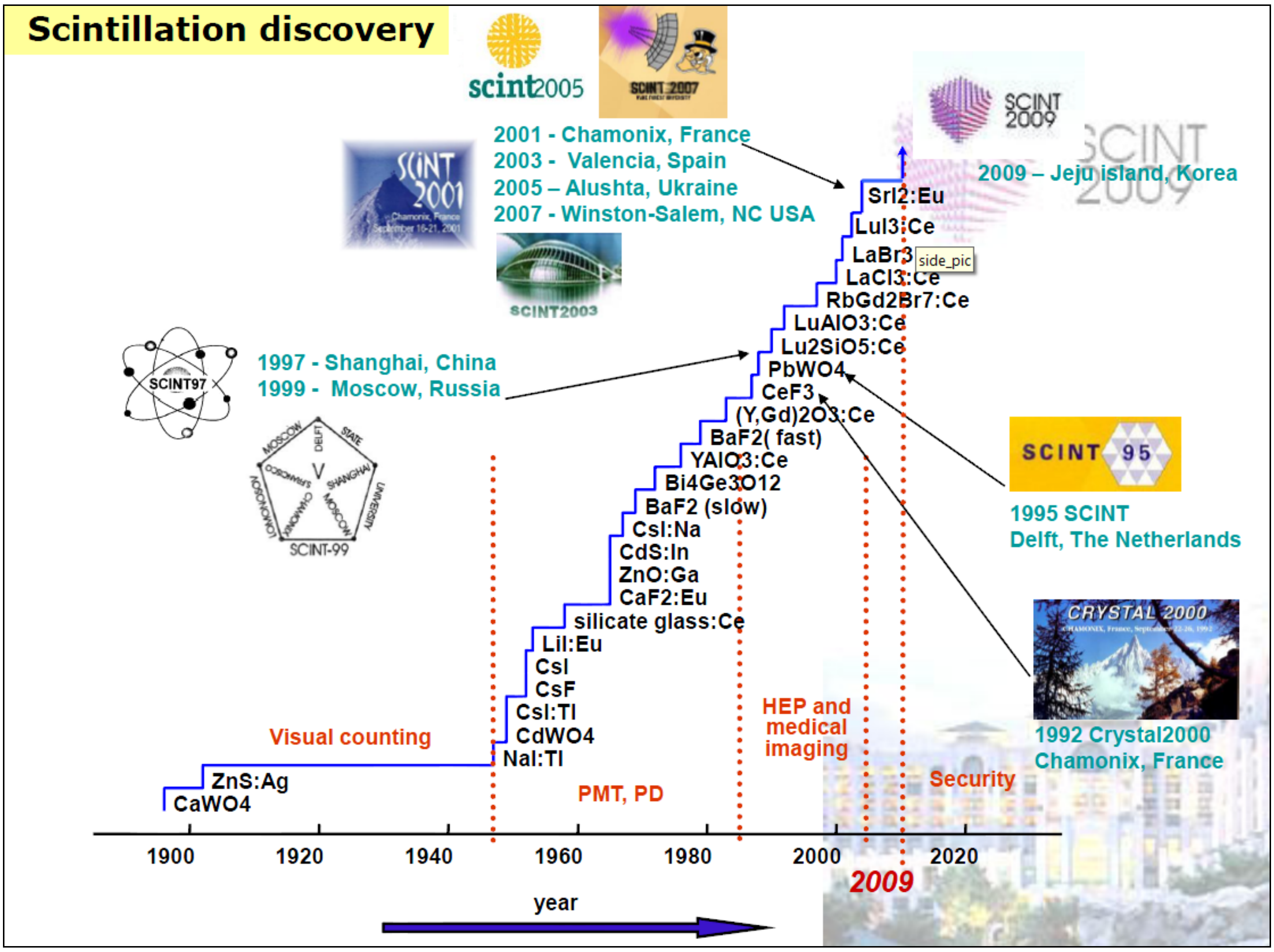



**Table 4 : Scintillation history; extracted from ISMA's presentation made at the SCINT 2009 conference**

The **earliest scintillators** included CaWO4 that was used for the first time in the year following Roentgen's discovery of X-rays ; uranyl salts used by Becquerel in 1896 to discover radioactivity; ZnS used by Crookes and by Rutherford to study alpha particle scattering.

**The first phase** of scintillators and luminescent materials science started in 1903 when above mentioned Sir William Crookes used a scintillator to build a device on the base of a ZnS (zinc sulphide) screen to detect and count radioactivity. The scintillations produced by the screen were visible to the naked eye if viewed by a microscope in a darkened room; the device was known as a spinthariscope. The technique led to a number of important discoveries but was obviously tedious.

This period of **visual scintillation counting** ended with the development of the photomultiplier tube PMT. Indeed, scintillators gained additional attention in 1944, when Curran and Baker replaced the naked eye measurement with the newly developed PMTs to convert the weak light flashes into usable electric pulses that could be counted electronically. Counting by eye became obsolete and Curran&Baker's discovery marked the birth of the modern scintillation detector.


**Robert Hofstadter**

The science of scintillators and luminescent materials had entered into **second phase** five years later, in 1949 when sodium iodide doped with thallium (NaI(Tl)) was found by **Robert Hofstadter**[2] and colleagues to produce scintillation from incident ionizing photon radiations. NaI(Tl) was patented as a first scintillation material In 1950, John Harshaw from Harshaw Chemical Company (US), initiated interest in growing NaI(Tl) crystals by the Stockbarger method. NaI(Tl) is still the most widely used scintillation material and has the highest light yield of the commonly used scintillators. The spectre of its applications is quite large and comes from nuclear physics and nuclear medicine to geophysics and environmental measurements. Harshaw Chemical Company rapidly became a key actor of the scintillation and luminescence materials science and the worldwide leader in the development and supply of commercially available scintillation radiation detectors, namely with sodium iodide (thallium-activated) and others, thermoluminescence (TL) materials such as lithium fluoride, calcium fluoride and related thermoluminescence dosimetry (or TLD) instruments and systems.

One unique application for large NaI(Tl) crystals has been the configuration(s) termed "crystal ball." One such configuration constructed for the Stanford Linear Accelerator comprised several hundreds of NaI(Tl) pyramidal crystals in a spherical array approximately six feet in diameter with a photomultiplier tube mounted on each crystal. The crystal ball was then deployed in a collider beam in the accelerator looking at the interaction of high-energy nuclear particles and the resultant reaction.

In a burst of exploration during the following few years, the scintillation properties of most pure and activated alkali halide crystals were investigated. Lithium-containing compounds used to detect neutrons and the first glass scintillators (activated with cerium) were also developed in the 1950s. A steady precession of new scintillator materials followed including the discovery of very fast (600 ps) core–valence luminescence in BaF2.

**A third phase**—the past two decades—has witnessed a veritable renaissance in research and development of scintillator materials, prompted to a major degree by the need for scintillators for precision calorimetry in high-energy physics and for high-light-output scintillators for medical imaging, geophysical exploration, and numerous other scientific and industrial applications. A sense of the activity during the past decade can be gleaned from the proceedings of a series of conferences devoted to scintillator research and development, namely the Crystal 2000—International Workshop on Heavy Scintillators for Scientific and Industrial Applications—Chamonix (1992), the Materials Research Society Symposium on Scintillator and Phosphor Materials— San Francisco (1994), followed by the biannual Inorganic Scintillators and Their Applications conferences (SCINT 95—Delft, SCINT97—Shanghai, SCINT 99—Moscow, and SCINT 01—Chamonix. In addition to the materials noted in the scheme, other material developments included cerium-

[2] American physicist, winner of the 1961 Nobel Prize in Physics for the pioneering studies of electron scattering "in atomic nuclei and for his consequent discoveries concerning the structure of nucleons" (source: Wikipedia)

activated heavy-metal fluoride glasses, a dense chalcogenide $Lu_2S_3$:Ce, and $LiBaF_3$ and $Li_6Gd(BO_3)_3$:Ce for neutron detection. In the meantime, other scintillation crystals have been developed, namely by the above mentioned Harshaw Chemical Company to meet various customer needs and applications : CsI(Tl), CsI(Na), $BaF_2$, $CaF_2$:Eu, LiI:Eu, PbF, and others. The 6LiI:Eu is used for neutron detection, the $BaF_2$ (pure) is an example of a high atomic number (Z) photon detector and PbF2 is an excellent Cherenkov radiation detector. More recently Bismuth Germanate (BGO) has been developed for some specific applications. The positive properties of BGO include no need to be canned and it maintains its polish. Recently lead-halide-based perovskite-type organic/inorganic hybrid compounds yielding excitonic luminescence of a semiconductor with decay time constants of 100 ps have been reported.

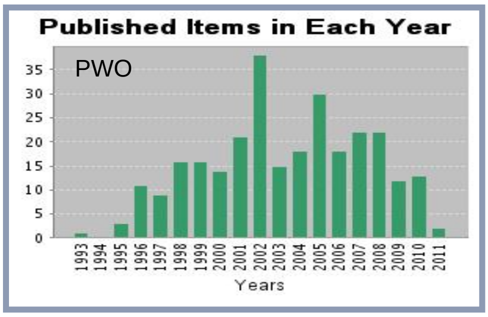
The discovery of $PbWO_4$ (PWO) by L.L. Nagornaya from the Institute for Scintillation Materials of Ukraine led to the revolution in the collider physics and created a base for the new generation of detection systems in high energy physics, starting from a calorimeter for CMS (LHC, CERN) and finishing with the project PANDA (DSI).

Ce activated crystals $LaBr_3$ and $LaCl_3$ with light yield close to theoretical limit and high energy resolution has been developed in Delft University in The Netherlands. Now these materials are applied in radiation detection devises with high resolution.

The rapid development of the Medical imaging systems in the early 80, namely of the single photon emission computed tomography (SPECT) and positron emission tomography (PET), with the increasing requirements for medical imaging equipment, boosted the demand for the scintillators as the radiation detection materials. A typical example is BGO, which has become the main component of PET scanners since the large effort made by the L3 experiment at CERN to develop low cost production methods for this crystal. $Lu_2SiO_5$:Ce (LSO:Ce) and LYSO:Ce with higher density than halide crystals, high light yield and fast decay time are found and used as scintillators in PET systems, but they are expensive and possess strong afterglow. Cheeper and improved materials are still needed. For this purpose in the resent years solid solutions are studied like mixed Lu, Gd, Y oxyortosilicates, (Lu, Y) and (Al, Ga) garnets, Ba, Sr, Cs mixed halides with different halide anions ($F^-$, $Cl^-$, $Br^-$, $I^-$).
After September 11th 2001, the US funds are redirected toward « homeland security ». Desired properties of scintillators are energy resolution, density, but decays are a bit less important. Intensive development of systems for homeland security needs for cheep scintillators with high light yield and resolution stimulate renaissance of Eu-doped halide scintillators like as NaI:Eu, $SrI_2$:Eu, BaBrI:Eu, $CsBa_2I_5$:Eu.

Concurrent with the materials developments, the use of **synchrotron radiation and laser spectroscopy** has led to a greater understanding of the complexities inherent in exciton and defect formation and the numerous processes involved in scintillation. These physical processes are now generally well understood (although details of some specific materials may still be lacking).

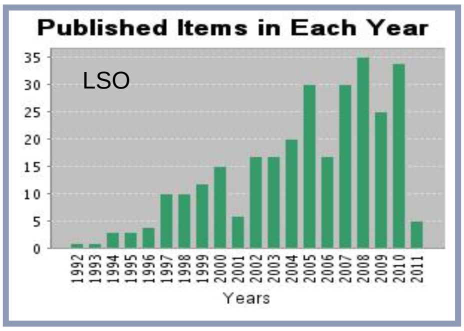
Today, new applications dictate research directions, in other words, not the results of fundamental scientific discoveries, but the demands of the society to have principally new technical solutions and effective sensor materials for these solutions are considered to be the driving power. As an example some correlations of scientific activity vs. new applications demands are listed below.

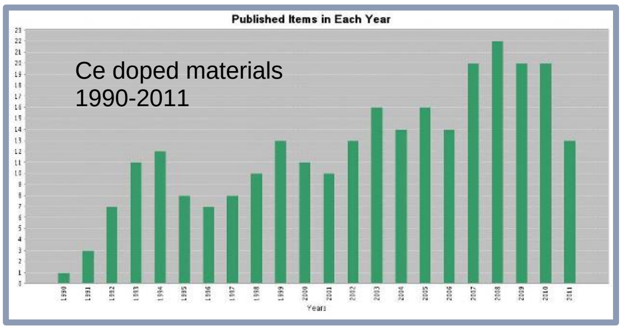



90's: A new material is needed for CMS in High energy physics (/BGO was used in L3).

**Requirements:** high density, fast decay, yield, mass production capability
$PbWO_4$ and $CeF_3$ appear rapidly as candidates
$PbWO_4$ won
Up to 1997, activity on $PbWO_4$ and then it decreases

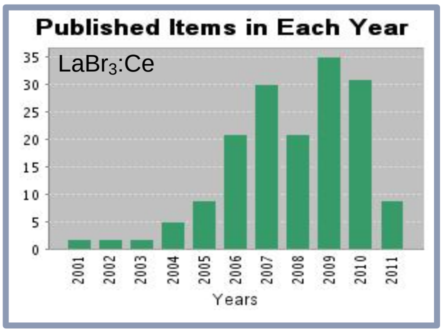
At the same time: discovery of LSO:$Ce^{3+}$, for **oil drilling**, but it is also of **interest for PET imaging** (medical application= $ -> industrial interest)

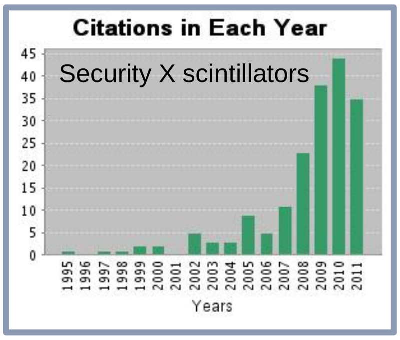



Up to 2005: activity on denser materials (Lu based) doped with $Ce^{3+}$ (fast) for PET

One of the **required performances for PET** was the energy resolution correlated to the scintillation yield:
$LaBr_3$, $LaCl_3$ doped $Ce^{3+}$ are found (high yield and resolution but hygroscopic, fragile and expensive). In parallel, new photodetectors appear.




Extracted from C. Dujardin presentation, IWASOM, Poland, 2011

Motivation of the search and development starts from the social demands of the society in whole (for instance, demand for safety assurance and antiterrorist systemic activities, development of the medical care and so on), proceeds to the chain of the global projects (for example, collider projects for high energy physics, astrophysical cosmic telescopes, medical systems for molecular imaging and others) and finishes with the engineering requirements of the advanced radiation registration systems (calorimeters and bolometers, OFEKT, KT and PET systems, radiation portals and active inspection systems, geophysical equipment and ecological monitoring systems).

The active steps of the specialists in the field of scintillation material science start exactly from the last stage. They have well-defined methodology and consequence of the activities: at first dominates the search and choice of the optimal scintillation medium itself, then the row of technological developments and production of the scintillator is carried out. Finally, the last stage is the maximum perfection of the scintillation detector. There are two main factors throughout these stages: the cost of the development and the time for its realization.

If in the middle of the previous century it took 20 years to develop a perfect scintillation material (for instance, NaI:Tl was discovered in 1949, but it has been produced large-scaled only since 1960s), recently the time has been sharply reduced (e.g. for LaBr3:Ce production it took only 3-4 years, LYSO became commercially available just in two years after the first publications, as opposed to its precursor LSO, whose production technology took more than 10-12 years).
Despite the social motivation of the developments, the scientific base remains the keystone of today's scintillation material science.

Given the discoveries and investigations that have occurred during the past century, today we have a wide variety of well-characterized inorganic scintillation materials for various applications— oxides, halides, and chalcogenides; crystals, glasses, and ceramics [20]. One may therefore ask whether there are better scintillators still to be discovered. If so, how are we going to find them? What do we mean by better? How much better can scintillators be? Have we exhausted the periodic table?

It should be noted, that most applications desire the same properties for an ''ultimate'' scintillator (high density and atomic number, high light output, short decay time without afterglow, convenient emission wavelength, mechanical ruggedness, radiation hardness, and low cost), but the lack of a perfect material has resulted in a number of different scintillators being developed and used. For each application some properties of scintillators are important but some are not critical. So, one can select the ''better'' appropriate scintillator from a wide variety of known scintillation materials. On the other hand, it’s a stimulus for further investigation.

What one means by ''better'' varies with the application. The scintillation researcher must be mindful of numerous considerations in the pursuit of ''better'' for a specific application. The needs vary. The scintillation wavelength and the light yield will determine the best photodetector to use (e.g., photomultiplier tube, photodiode, and avalanche photodiode). Whereas for detecting very energetic particles light yield may not be too critical, for applications where the particle energy is smaller or fixed, increased light yield is important for improving accuracy and spatial resolution. Energy resolution and proportionality also depend on light yield. Fast signal rise and decay times are important for good timing resolution and high counting rates or for time-of-flight modes of operation. The absence of after-glow is important in medical imaging. Stability includes several factors that must be known or controlled: environmental or chemical durability, ruggedness and mechanical shock resistant, and variation of light output with temperature and time. Insensitivity to air, moisture, and light and the absence of weak cleavage planes in crystals are highly desirable characteristics. Radiation damage, which may be irrelevant for detectors for most imaging applications, is extremely important in high radiation environments such as in detectors for use with high luminosity colliders. High density and stopping power (i.e., large effective atomic number) are important for reducing the amount of scintillator material needed.

For neutron detection, a constituent ion with a high neutron absorption section such as 6 Li, 10B, or 157Gd is necessary. The scintillation material may be a crystal or glass in bulk, fiber, or sheet form. The price of raw materials and the method of producing and fabricating the material into the desired size and shape all enter into the final cost. These and other factors differ in their relative importance in selecting better materials for a particular application.
A lot of new scintillators have been discovered in resent years (table 5), but their mass production it is the challenge for the future.

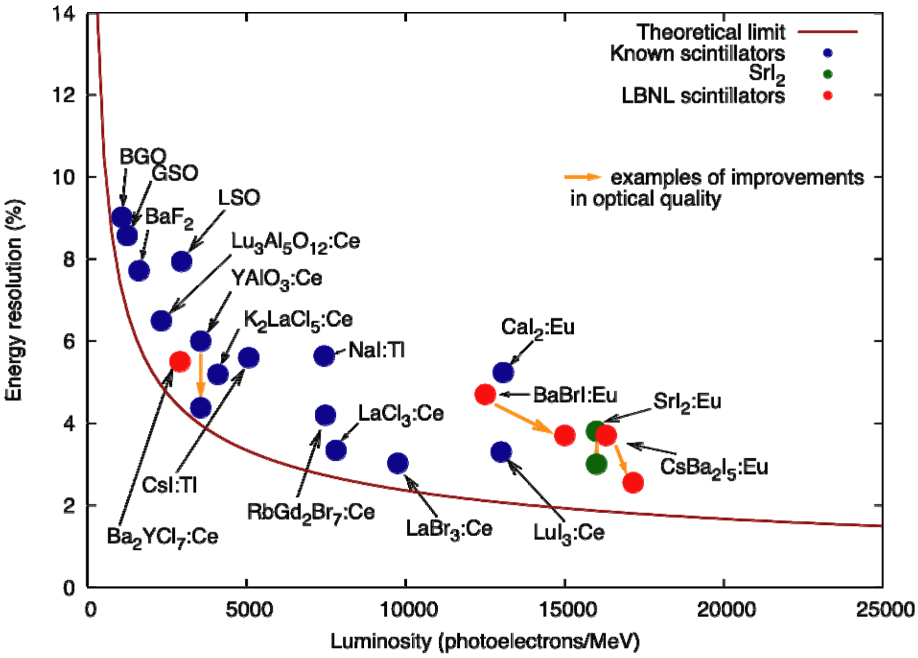
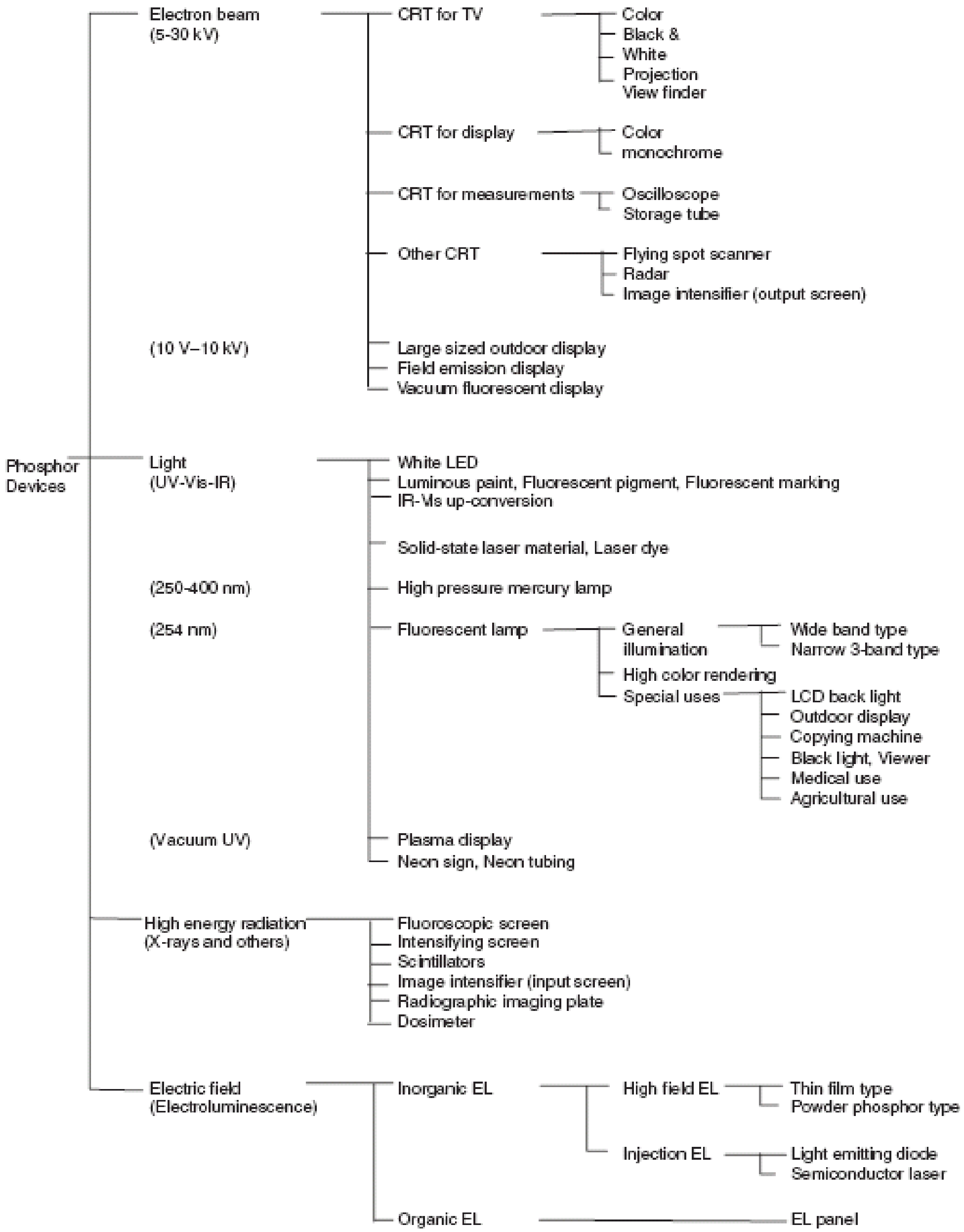



Table 5 : Extracted from E. D. Bourret presentation, Workshop Nuclear Medicine, Physics, Engineering and Practice, 2011, Kharkov, Ukraine .

## 2.3. Application of Luminescent Materials and Scintillators

Luminescent Materials cover a wide range of materials and applications that are of current interest including organic and inorganic light emitting materials, nanomaterials, powder and thin-film phosphors and devices (table 6 Phosphor Devices, extracted from Phosphor Handbook, M.Weber).

Table 6. Phosphor Devices




The applications of phosphors can be classified as: (1) light sources represented by fluorescent lamps; (2) display devices represented by cathode-ray tubes; (3) detector systems represented by X-ray screens and scintillators; and (4) other simple applications, such as luminous paint with long persistent phosphorescence. Another method to classify the applications is according to the excitation source for the phosphors. The table lists various kinds of phosphor devices according to the method used to excite the phosphor. It gives a summary of phosphor devices by the manner in which the phosphors are applied.

As one can see from this Table luminescence phenomenon and Luminescent materials are extensively used in a great number of application domains.

**The interest of the SUCCESS project lies in the area of photo- and radio- luminescence, but the special emphasis put on high energy radiation detection.** Why is it so important for an average person or society?

Scintillators are necessary in many applications of our life and modern technology, ranging from science to efficient and precise radiography imaging methods in medicine, security and industry.
Therefore, developments in the field of nuclear instruments and methods that were observed in the recent years have been largely related to demands of current technologies in application domains. The figure below summarized key application domains of scintillators.

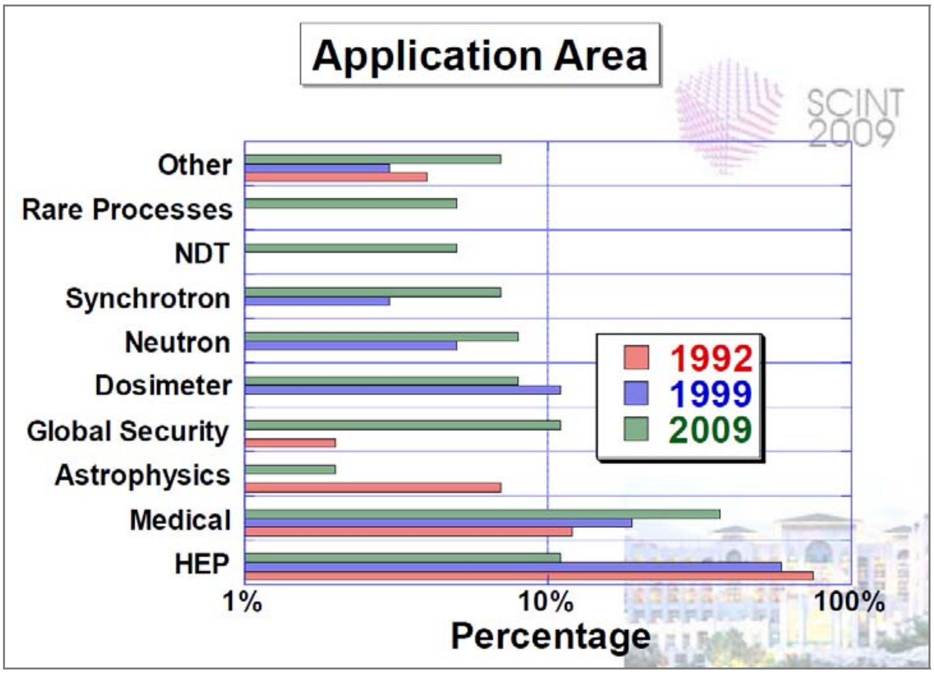



**Table 7 : scintillators application domain,**
**extracted from ISMA presentation at the SCINT 2009 conference**

### *2.3.1. Nuclear Medicine*

**Table 8: Gamma camera**

Rapid increase in the number of patient suffering from cancer is an acute problem for all industrially developed countries including Japan. However, cancer can be treated and successfully cured if found at the early stage. Nuclear medical imaging systems are a very effective tool in cancer diagnosis. Because cancer cells grow fast, it consumes much more glucose than healthy ones. If a chemical analog of glucose-fluorodeoxyglucose marked with the positron emitter 18F is prescribed to a patient with cancer, cancer cells emit higher level of radiation which can be detected with Nuclear medical imaging system providing an image of a cancer tumor.

There are several types of medical imagine devices, which distinguish on source of excitation, signal detection principles and appropriately on diagnostic capabilities. For example: Computer Tomography (CT) use X-rays, allow obtaining of high resolution image. Positron emission Tomography (PET), Single Photon Emission Computed Tomography (SPECT) and Gamma camera use radionuclide radiation (positron emitter $^{18}F$ for PET, $^{99}Th$ and others) and provide information about the processes into alive body.

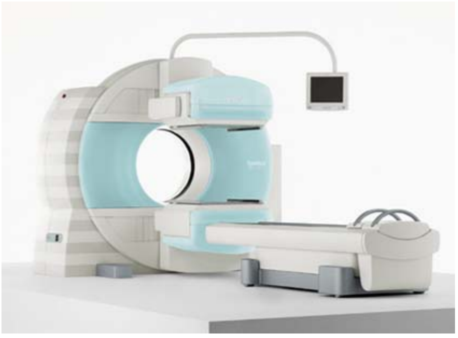


**Table 9: Single Photon Emission Computed Tomography (SPECT)**

**Multimodality imaging PET/CT, SPECT/CT** combines high spatial resolution of anatomical imaging of Computer Tomography (CT) and informational content of organs functionality by Positron emission Tomography (PET).

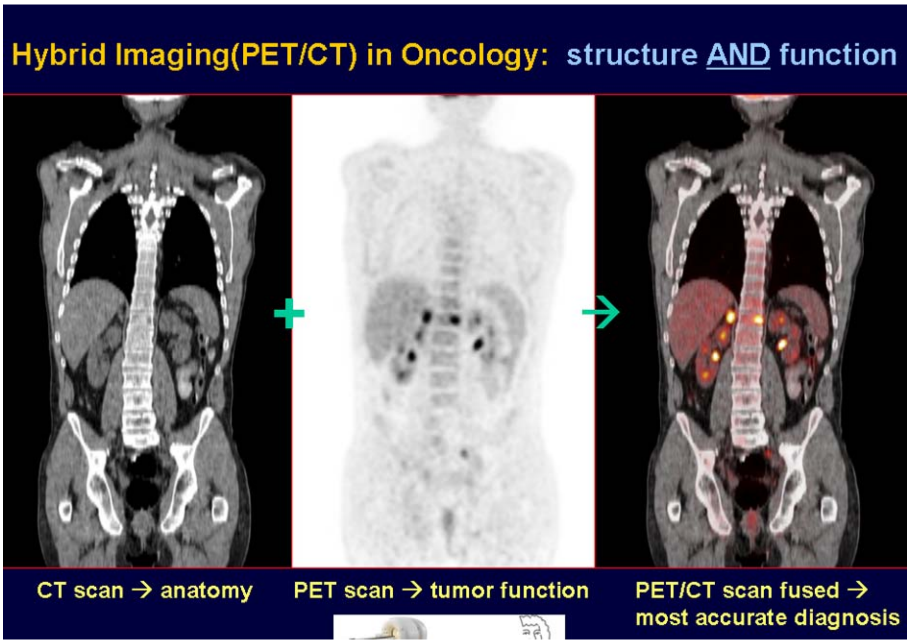



**Table 10: Extracted from C.A. Hoefnagel presentation, Workshop Nuclear Medicine, Physics, Engineering and Practice, 2011, Kharkov, Ukraine .**

Besides clinical oncology medical imaging systems are used in cardiology, neurology and psychiatry. Nuclear medicine methods can be used not only for humans, but for small animals. 3D resolution ~1mm for small objects can be achieved.

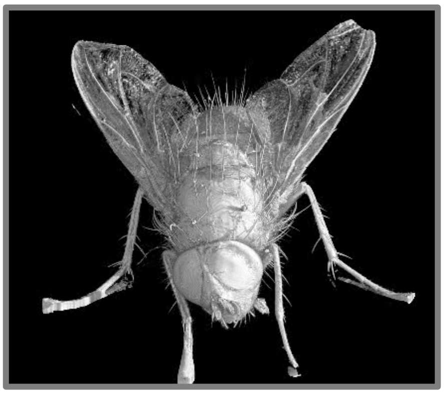


**Table 6 : X-ray Tomography: LPE, LuAG:Eu3+**

Requirements to scintillator for PET: Fast decay is needed for fine coincidence detection, scintillation yield allow to obtain good resolution, high density allow to minimize size of detector.

$BiGeO_4$ (BGO), $Lu_2SiO_5$:Ce (LSO:Ce) and Lu(Y)$SO_5$:Ce (LYSO) are used for PET systems. BGO have high density (7.13 g/cm$^3$) and low price but low light yield (decay 300ns, 8000ph/MeV). $Lu_2SiO_5$:Ce (LSO) and LYSO possess (higher light yield (25000ph/MeV,) and fast decay time40ns), but they are more expensive.

**Possible evolution :**

- to use new fast scintillator with higher light yield and resolution
- to use Time of flight technique for noise reduction (Require time resolution <200ps depends on the whole chain crystal-photodetector-electronic and light collection)

Detector manufacturers as well as end-users face a tremendous cost pressure. This creates a demand for reliable high quality scintillators at an affordable price.

**Computer Tomography (CT)**

The scintillators CsI:Tl and $CdWO_4$ are currently used as single crystal detectors in commercial **CT scanners**. Examples of commercial ceramic scintillator materials are $(Y,Gd)_2O_3:Eu^{3+}$ and $Gd_2O_2S:Pr^{3+}$.

**Main requirements to scintillator:** density, yield, low afterglow level.

A good scintillator has to absorb as many X-ray quanta as possible in order to keep the quantum noise as low as possible. On the other hand, the conspicuity of fine details is important for a good diagnosis. Thus, the lateral light spreading in the conversion layer has to be minimized. This is very important to achieve a good low contrast resolution. If image quality is lost during the X-ray conversion process, no electronics or software can restore it.

**Evolution:** to use screens with micro-needles of CsI:Tl. Low density are acceptable since needles act as waveguides

Developments in X-ray excited phosphors include materials with much greater X-ray stopping power and better conversion efficiency. This greatly reduces the patient exposure needed for a good quality picture.

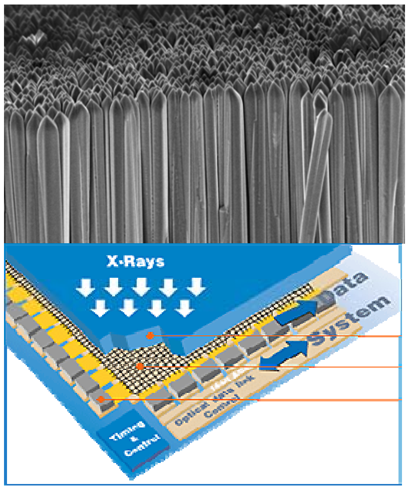



**Table 7 : screens with micro-needles of CsI:Tl (Siemens)**

**SPECT** claims for large size crystals ( size ~ 600x500x9.5 mm) with high performance. Electronics and image correction can just only improve SPECT performance but not to compensate the scintillator "faults". Detector operation life is 7-9 years, so radiation resistance is advisable.
NaI(Tl) has optimum «price/quality». NaI:Tl is commonly used for SPECT scanners.

---

**Large size detector claim for industrial technology development**
**Clinical imaging needs improved signal to noise ratio and spatial resolution near the theoretical limits**

---

### *2.3.2. Security applications*

**Homeland security** is an umbrella term for security efforts to protect country against terrorist activity. The scope of homeland security includes:

- **Border security, including both land, maritime and country borders;**
- **Transportation security, including aviation and maritime transportation;**
- **Detection of radioactive and radiological materials;**
- **Research on next-generation security technologies.**

Table 8 : luggage screening machine

**Scintillation counters** are used for detection of potentially dangerous neutron or/and gamma-emitting materials during transport. These include scintillation counters designed for freight terminals, border security, ports, weigh bridge applications, scrap metal yards and contamination monitoring of nuclear waste. There are variants of scintillation counters mounted on pick-up trucks and helicopters for rapid response in case of a security situation due to dirty bombs or radioactive waste. Hand-held units are also commonly used. Scintillators are used in the airport luggage screening machines shown in the figure. Its principle of operation is similar to the medical X-ray equipment.

**Passive systems are used for** source detection, radioactive isotops identification and classification.

**Active scaners** allow to obtaine image of even moving objects.

NaI:Tl, $LaBr_3$:Ce, $CdWO_4$, BGO and plastic scintillators are the common materials. LiI :Eu is used for neutrons detection.


**Table 9 : examples of passive (left) and active (right) commercial instruments**
**(Extracted from Z.Bell presentation, SCINT2009, Korea.)**

Nuclear weapons, plutonium (239Pu) and enriched uranium (235U, 233U) have to be selected from background counting, well logging (252Cf) and medical (99Th) isotopes

## Implications for scintillators development

- **Resolution**
  - Drives identification algorithms
  - High resolution makes peak-searching attractive
  - Shielding makes peak-searching UNATTRACTIVE
  - Modeling the full spectrum may make 2 – 3% good enough
  - Energy windows on plastic scintillator spectra (20-30% resolution) distinguish SNM from NORM
- **$Z_{eff}$**
  - Higher values favor peak-searching
  - Values ~50 provide good photoelectric cross section
  - High-energy capture γs favor high $Z_{eff}$ for pair production
  - 10% change in $Z_{eff}$ results in 30% change in PE cross section
  - But from 1 – 4 MeV, mfp ~ 15/ρ, independent of Z
  - Compton imaging favors LOW $Z_{eff}$

- **n/γ discrimination**
  - Separate neutron and gamma sensitivity desirable
  - $>10^4$:1 discrimination needed in single detector
    - Gammas mistaken for neutrons cause false alarms
    - Enables simultaneous imaging
    - Decreases component count/footprint
    - Fast neutrons:
      - Organic liquids can do this now
      - Organic crystals (stilbene, anthracene…)
- **Size**
  - Hand-helds need 30-50 $cm^3$
  - Portal monitors need $10^3$ – $10^5$ $cm^3$
  - CTE and fracture toughness affect maximum size (will a 10x10x40 cm $LaBr_3$ survive vibration and temperature?)
  - Transparency needs to be commensurate with size
    - PMT and scintillator axis tend to be collinear
    - Plastic scintillator has 100 cm mfp

- **Linearity**
  - Effects important below 150 keV
  - Shielding preferentially attenuates these energies
  - Probably NOT tremendously important
- **Speed**
  - Active interrogation
    - Low afterglow extremely important
      - Prompt fission n/γ outnumber the delayed
      - < 1 μs good
      - < 100 ns highly desirable
      - Successive radiographic images must not bleed over
    - Fast decay time important for multiplicity measurements
    - Fast rise time important for coincidence/timing measurements
  - Passive
    - Detector is always flux-starved
    - ns decay time NOT required

- **Cost**
  - NaI: ~US$10/$cm^3$
  - CsI: ~US$20/$cm^3$
  - $LaBr_3$: ~US$500/$cm^3$
  - "Standard" Plastic: ~US$0.25/$cm^3$
  - "Special" Plastic: Comparable to NaI
  - $1000/unit in a hand-held → crystal can't cost $300!

### Requirements

- Passive
  - Energy Range
  - Time to detect
  - Resolution
  - Efficiency
  - Directionality
  - Temperature Range
  - n/γ Discrimination
- Active
  - Spatial Resolution
  - Temporal Resolution
  - Afterglow
  - Radiation Damage Resistance
  - Temperature Range

**Scintillators for security systems should have follow characteristics:**
**high light yield and resolution, good n/γ discrimination, ns decay time not required (for passive systems), low costs for mass production.**

### *2.3.3. Particle and high energy physics*

**Dark matter search**

Scientists using different methods to determine the mass of galaxies have found a discrepancy that suggests 90% of the universe is matter in a form that cannot be seen. A dark matter discovery could possibly affect our view of our place in the universe. Some scientists think dark matter is in the form of massive objects, such as black holes, that hang out around galaxies unseen. Other scientists believe dark matter to be subatomic particles that rarely interact with ordinary matter.

What do scientists look for when they search for dark matter? We cannot see or touch it: its existence is implied. Possibilities for dark matter range from tiny subatomic particles weighing 100,000 times less than an electron to black holes with masses millions of times that of the sun. The two main categories that scientists consider as possible candidates for dark matter have been dubbed MACHOs (Massive Astrophysical Compact Halo Objects), and WIMPs (Weakly Interacting Massive Particles). Astronomers search for MACHOs and particle physicists look for WIMPs. WIMPs are the little weak subatomic dark matter candidates, which are thought to be made of stuff other than ordinary matter, called *non-baryonic* matter.

All hope of proving WIMPs exist rest on the theory that, on occasion, a WIMP will interact with ordinary matter. Because WIMPs can pass through ordinary matter, a rare WIMP interaction can take place inside a solid object at low temperature. The trick to detecting a WIMP is to witness one of these interactions. Expected counting rate<< 1count/day and per kg of detector and a energy deposition between 45 et 55 keV!!!! It is in the competition with natural background (neutron, b, g).

**Discrimination between electromagnetic particles, neutrons and WIMPs is necessary.** Photons and $\beta$ give ionization while WIMPs and neutrons interact with nucleus (recoil), so the ratio between photon signal/ phonon signal depends of the incident particle. For neutron / WIMP discrimination the interaction with nucleus of various mass is applied. Combination of several scintillating compositions and detectors allow to resolve problem of discrimination $\gamma$, $\beta$, neutrons and WIMPs.

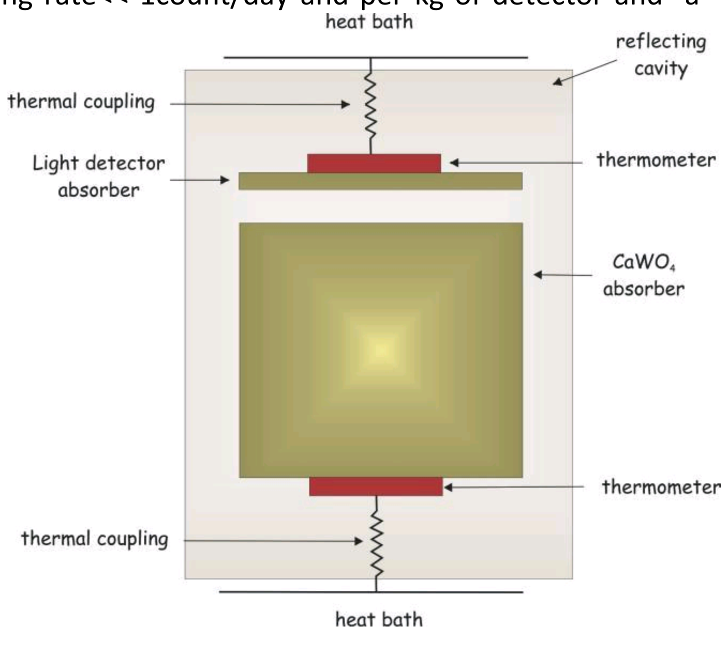



**Table 10 : Calorimeter for WIMP detection**

There are several current projects on Dark matter: DAMA, CRESST-II, Belle-II, EDELWEISS, EURECA and others.

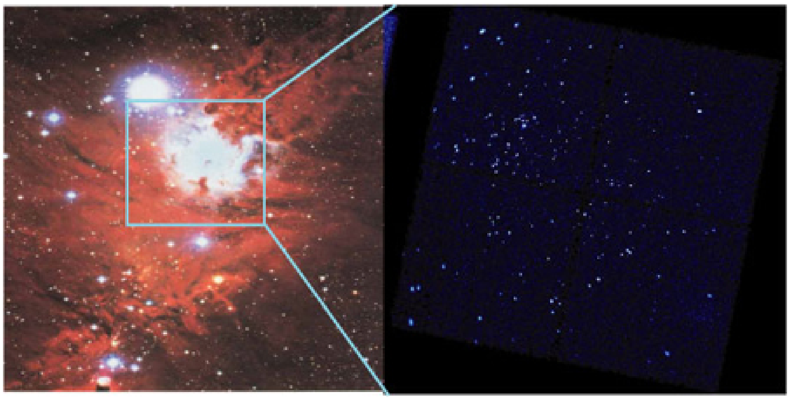
The *DAMA project* at the Gran Sasso National Laboratories is an observatory for rare processes and use of large mass highly radiopure scintillator set-ups (~100 kg highly radiopure NaI(Tl). The second generation DAMA/LIBRA set-up (Large sodium Iodide Bulk for RAre processes; ~250 kg more radiopure NaI(Tl)) with a larger mass and an increased sensitivity is continuing the investigations of DAMA/NaI set-up. Finally a 3-rd generation R&D toward the creation of a possible 1 ton NaI(Tl) set-up is in progress[3].

The *CRESST-II* is aiming at development of a cryodetector (temperatures below 10 mK) based on scintillating $CaWO_4$ crystals as absorbers. In this crystal a particle interaction produces mainly heat in the form of phonons, as for sapphire. But in addition a small amount of the deposited energy is emitted as scintillation light. Therefore when a second, smaller calorimeter is added to detect this light, most common backgrounds can be eliminated through their light signal. In tests this system was found to give very efficient active background discrimination (http://www.cresst.de/cresst.php)

*Demands to the crystals* : radio-isotope purity, Scintillation at low T (few mK), homogeneity of properties (1 ton?), low cost.

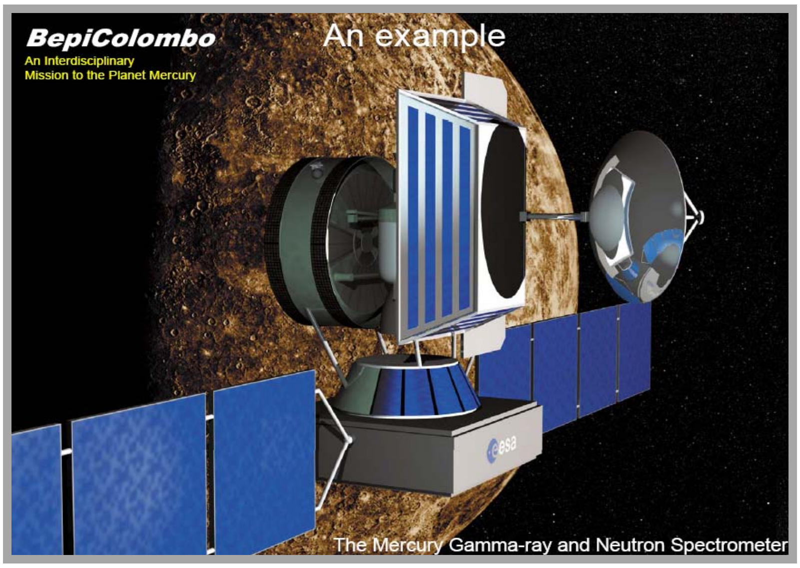
Crystals CsI, $Al_2O_3$, LiF, $CaWO_4$, BGO are under study.

### 2.3.4. Astrophysics



Scintillators are frequently used in astrophysics. Stars are born in dense and thick molecular gases observed in the optical wavelength. The upper left figure shows an image of massive star forming region NGC2264 where stars are blocked behind the expanding gas. However, newly-born stars emit intense X-ray radiation passing through the gas and with help of scintillators they can be clearly distinguished, see the upper right figure.

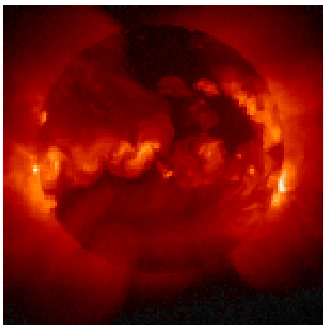
3 http://www.lngs.infn.it/lngs_infn/index.htm?mainRecord=http://www.lngs.infn.it/lngs_infn/contents/lngs_en/research/experiments_scientific_info/experiments/current/dama/




**Gamma-ray and neutron spectrometer on BepiColombo** spacecraft will provide the best understanding of Mercury to date. It consists of two individual orbiters: the Mercury Planetary Orbiter (MPO) to map the planet, and the Mercury Magnetospheric Orbiter (MMO) to investigate its magnetosphere. $LaBr_3$:Ce is chosen as the best candidate for Gamma-ray detection and LiI:Eu - as neutron detector.

CsI:Tl, stilbene, $LaBr_3$:Ce, $LaCl_3$:Ce, LuYAP:Ce, paraterphenyl, $Cs_2LiYCl_6$:Ce (CLYC), $Cs_2LiYBr_6$:Ce (CLYB) are under study.

**The Solar Neutrino Problem**



Fusion reactions in the core of the Sun produce a huge flux of neutrinos. These neutrinos can be detected on Earth using large underground detectors, and the flux measured to see if it agrees with theoretical calculations based upon our understanding of the workings of the Sun and the details of the Standard Model (SM) of particle physics. The measured flux is roughly one half of the flux expected from theory. The cause of the deficit is a mystery. Is our particle physics wrong? Is our model of the Solar interior wrong? Are the experiments in error? This is the "Solar Neutrino Problem".

There are precious few experiments that seem to stand in disagreement with the SM, which can be studied in the hope of making breakthroughs in particle physics. The study of this problem may yield important new insights to help us go beyond the Standard Model. There are many experiments in progress, so stay tuned: Borexino, Homestake Lab, SAGE, GALLEX, SNO, KamLAND, Super-Kamiokande.

Heavy water, Ga and liquid scintillators are used for neutrino detection.

### *2.3.5. Hunting for mineral resources*

**Gamma ray logs** measure radioactivity to determine what types of rocks are present in the well. Because shales contain radioactive elements, they emit lots of gamma rays. On the other hand, clean sandstones emit very few gamma rays.

Scintillators are employed to discover oil or mineral resources. It was found that layers with excessive content of radioactive isotopes exists near the oil strata. The radiation informs us the position of the oil pool, and one can drill precisely without any wasting.

LSO, $CaF_2$:Eu, NaI:Tl are commonly used.

**Scintillators used in such environment should possess sufficient mechanical strength in addition to high light yield and fast decay**

### *2.3.6. Safety of nuclear plants and environment monitoring*

Scintillators and luminescence materials are a core part of the radiation measurement equipment – monitors, systems and radiation instruments that is used for varying purposes in radiation detection and monitoring. A nuclear power plant requires means for monitoring and controlling its processes and special equipment, instrumentation and control system, water radiation control ask for water dosimeter and spectrometer able to monitor running , drinking water, identify and measure a specific activities of radionuclides. Such devices are used at the nuclear power plants as well for monitoring of waste water.
Radiation sensors, namely plastic scintillation detectors for a contamination monitor are widely used in radioactive surface contamination monitors, waste control systems, monitoring systems around nuclear power plants. All ***these systems require*** for different properties of scintillators, such as high density, fast operation speed, low cost, radiation hardness, production capability and durability of operational parameters. For example, particular proprieties of organic liquids ensuring increased neutron detection efficiency are used in scintillation counters.

Among the properties listed above, the light output is the most important, as it affects both the efficiency and the resolution of the detector (the efficiency is the ratio of detected particles to the total number of particles impinging upon the detector; the energy resolution is the ratio of the full width at half maximum of a given energy peak to the peak position, usually expressed in %). The light output is a strong function of the type of incident particle or photon and of its energy, which therefore strongly influences the type of scintillation material to be used for a particular application.
Radiation measurement equipment for environment monitoring use inorganic crystals that have been grown in high temperature furnaces (e.g. alkali metal halides) often with a small amount of activator impurity. The most widely used is NaI(Tl) (sodium iodide doped with thallium). Other inorganic alkali halide crystals are: CsI(Tl), CsI(Na), CsI(pure), CsF, KI(Tl), LiI(Eu). Some non-alkali crystals include: $BaF_2$, $CaF_2$(Eu), ZnS(Ag), $CaWO_4$, $CdWO_4$, YAG(Ce) ($Y_3Al_5O_{12}$(Ce)), GSO, LSO.

A disadvantage of some inorganic crystals, e.g., NaI, is their hygroscopicity, a property which requires them to be housed in an air-tight enclosure to protect them from moisture. CsI(Tl) and $BaF_2$ are only slightly hygroscopic and do not usually need protection. Addressing this disadvantage plastic scintillators (polymers like polymethyl methactylate with organic scintillants dispersed inside) receive increasing attention in development of sensors for environmental monitoring.

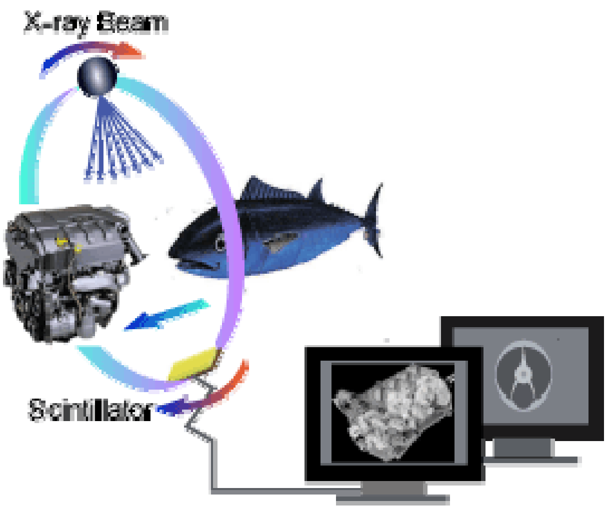
### *2.3.7. Non-destructive inspection*

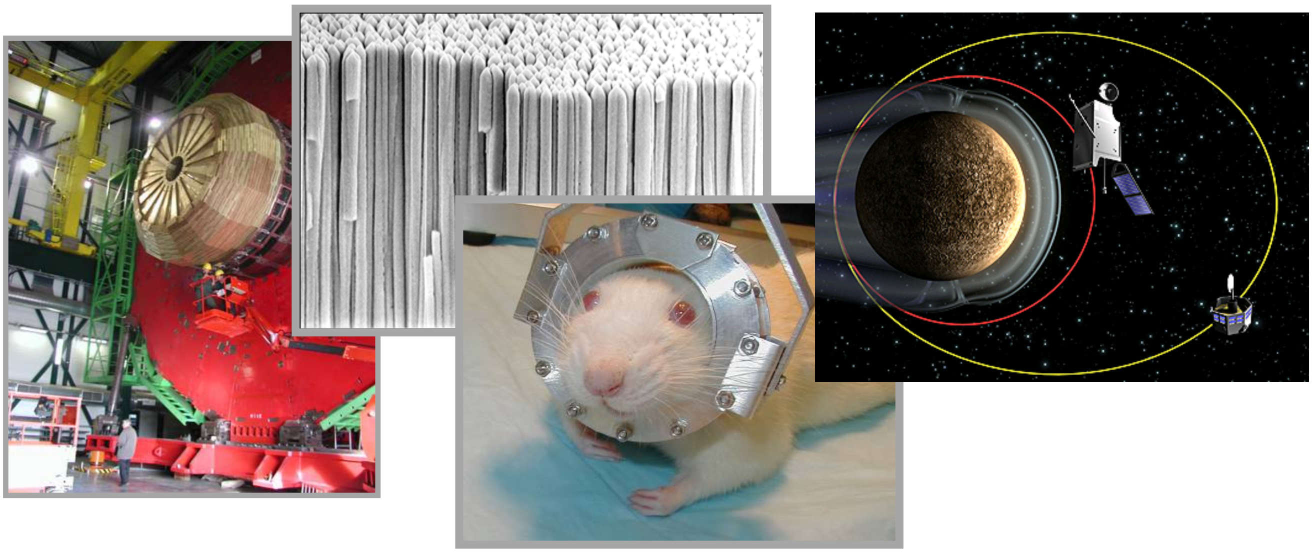
Various X-ray inspection systems with high resolution image enable both see-through and scanning 2D and 3D fine checking even when the object is moving.

High penetrating power of radiation enables us to examine different kind of materials including delicate cultural objects or even animals without destructing them.

Examples of thin films for X-ray imaging are

LuAG:$Eu^{3+}$, GGG:$Eu^{3+}$ (CEA LETI) (Thickness from 1mm to 25 mm) obtained by Liquid Phase Epitaxy; $Lu_2O_3$ et $Gd_2O_3$ doped with $Eu^{3+}$ (LPCML) (Thickness<1mm) obtained by Sol-Gel coating.





**Development and studies of materials for Scintillation applications are highly active area including several fields from materials science to imaging systems, medicine. This area has to be still developed.**

About 175 tons of scintillator are required annually and the demand for the various scintillators will increase significantly in the nearest future.

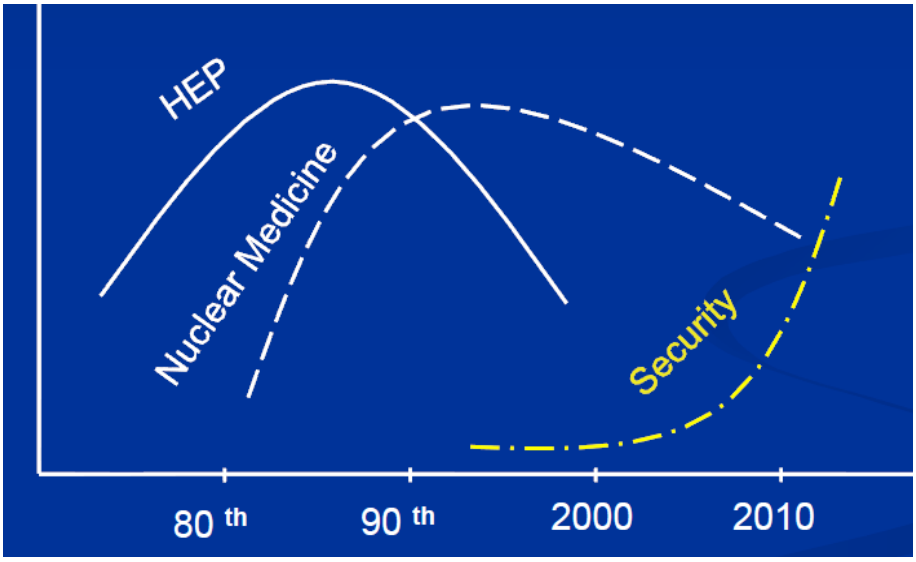



**Table 11** : **Trend of demand on Alkali Halide Scintillators (Extracted from A.Gektin presentation SCINT2009, Korea.)**

**The main application domains of scintillators are High Energy Physics, Nuclear Medicine and Security.**
**Performance/cost rate is the most important issue for the scintillator development.**