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Current Trends in Scintillator Detectors and Materials

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Abstract

The last decade has seen a renaissance in inorganic scintillator development for gamma ray detection. Lead tungstate ($PbWO_4$) has been developed for high energy physics experiments, and possesses exceptionally high density and radiation hardness, albeit with low luminous efficiency. Lutetium orthosilicate or LSO (Lu_2SiO_5:Ce) possesses a unique combination of high luminous efficiency, high density, and reasonably short decay time, and is now incorporated in commercial positron emission tomography (PET) cameras. There have been advances in understanding the fundamental mechanisms that limit energy resolution, and several recently discovered materials (such as $LaBr_3$:Ce) possess energy resolution that approaches that of direct solid state detectors. Finally, there are indications that a neglected class of scintillator materials that exhibit near band-edge fluorescence could provide scintillators with sub-nanosecond decay times and high luminescent efficiency.

Introduction

This paper attempts to summarize some of the recent developments in scintillator materials. 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 different applications [1, 2]. This paper briefly describes two such scintillation materials that have been developed in the past decade for use in high energy physics and nuclear medical imaging. The properties of one of these materials spurred the investigation of the fundamental mechanisms that limit energy resolution, and has lead to some newly discovered scintillation materials that have unprecedented energy resolution. Finally, there has been recent revived interest in a scintillation mechanism that appears capable of producing scintillation materials that are both fast and luminous.

Lead Tungstate

The present generation of high energy physics experiments requires levels of radiation hardness greater than 10^6 rads, a level unreached by existing materials. Short decay time is required because of the high bunch crossing (*i.e.* event) rate, but the high photon energies involved imply that materials with low scintillation efficiency can be used. The Crystal Clear

Collaboration initially developed CeF_3 to meet these needs [3]; CeF_3 possesses a light output of 4,000 photons / MeV, a decay time of 27 ns, and a 1.7 cm radiation length [4], but CeF_3 was discarded in favor of $PbWO_4$, which possesses a light output of 250 photons / MeV, a decay time of 5–15 ns, and a radiation length of 0.9 cm [5]. The motivation was the cost savings made possible by the shorter radiation length of lead tungstate. Modern high energy physics detector systems usually consist of a series of nested detectors, each a right circular cylinder and each optimized for different particle types. The diameter and height of the outermost detector is about 10 m. Dense scintillators are usually used for the electromagnetic calorimeter, which tends to be near the center of the system. A small reduction in the size of the central detectors leads to significantly reduced total system volume — a 1 cm reduction in the radius reduces the total volume by 5 m^3! Thus, although the scintillation properties of lead tungstate are inferior to cerium fluoride, lead tungstate was selected because its significantly shorter radiation length (0.9 cm versus 1.7 cm) allows the same absorption efficiency in a significantly shorter distance, which in turn allows a significant cost savings [6].

Significant effort has gone into the development of $PbWO_4$, primarily to understand its radiation damage mechanisms (color center formation on W vacancies, which can be significantly reduced by adding Nb^{5+} and Y^{3+} dopants), to maintain a consistent light output, and to develop reliable and economic growth methods for the large size crystals needed for calorimetry [7]. This development phase has recently ended and large scale production has begun, with approximately 10% of the 72,000 crystals needed for the CMS experiment complete [8].

Lutetium Orthosilicate

Many other applications, such as nuclear medical imaging, well logging, and treaty verification, desire to do gamma ray spectroscopy at high rates. There have been a number of Ce^{3+} -doped materials developed in the past decade that provide this, and lutetium based materials appear to yield particularly good properties [2]. The best known example is lutetium orthosilicate (usually known as LSO or Lu_2SiO_5:Ce), which has a light output of 25,000 photons / MeV, a decay time of 40 ns, and a density of 7.4 g/cc [9]. This material is particularly well suited for positron emission tomography (PET), a nuclear medical imaging technique that requires 511 keV photons to be detected with materials possessing short attenuation length, short decay time, and high luminous efficiency [10]. CTI PET Systems has spent several years developing this recently discovered material, again with the emphasis on maintaining consistent light output, and developing reliable and economic growth methods [9]. The development stage of this material is similar to that of lead tungstate — large scale production has recently begun and commercial PET cameras containing LSO have recently appeared on the market.

Non-Proportionality

One aspect of LSO's performance has puzzled researchers — although it has a high luminous efficiency, its energy resolution is significantly worse than is expected from counting statistics. Many alkali-halide scintillators (including NaI:Tl and CsI:Tl) also share this undesirable feature and there has been a recent revival in efforts to understand this effect. Figure 1 plots, for a variety of alkali-halide and non- alkali-halide scintillators, the energy resolution (for 662 keV gamma ray excitation) as a function of the mean number of photoelectrons produced [11]. With very few exceptions, the points lie considerably above the solid curve that shows the theoretical lower limit due to counting statistics, indicating that the energy resolution of most scintillators is worse than that predicted by counting statistics.

The present consensus is that the cause is non-proportionality — the luminous efficiency (*i.e.* the number of scintillation photons per unit energy deposit) of the scintillator depends on the energy of the particle that excites it [12]. A gamma ray begins the excitation process by creating a knock-on electron either by photoelectric absorption or Compton scatter. As this primary electron traverses the scintillator, it loses energy to the scintillator (exciting it) and also produces other relatively high energy electrons (delta-rays), which also excite the scintillator. Thus, the scintillator is effectively excited by a number of electrons with a variety of energies, even when the primary excitation source is a single gamma ray. If the luminous efficiency is independent of the electron energy, then the number of scintillation photons produced by two gammas with the same energy will be the same (within counting statistics) because the sum of the electron energies is the same (and equal to the incident gamma energy). However, if the luminous efficiency depends on electron energy, then the number of scintillation photons will not necessarily be the same, and these variations degrade the energy resolution.

This dependence of luminous efficiency on electron energy is measured using a Compton technique [12]. A scintillator is excited by a source of monochromatic gamma rays. Some will undergo Compton scatter in the scintillator, with the energy deposited in the scintillator (which is equal to the energy of the knock-on electron) equal to the difference between the incident gamma ray energy and the energy of the outgoing Compton scattered gamma ray. A high purity germanium detector (which has excellent energy resolution) measures the energy of the outgoing gamma ray (and thus the electron energy) and a photomultiplier tube coupled to the scintillator measures the number of photons produced. Since kinematics defines the relationship between the scattering angle and the energy of the outgoing gamma ray, different electron energies can be obtained with a single source by placing the germanium detector so that it observes gammas that scatter through different angles.

Figure 2 shows measurements of luminous efficiency versus electron energy for several scintillators [12]. Ideally, the lines should be horizontal, indicating no dependence on electron energy. Virtually none of the materials possess this ideal shape, and those (such as LSO, CsI:Tl, and NaI:Tl) that are significantly above the theoretical curve in Figure 1 also possess significant non-linearity (a steep slope in Figure 2, especially at higher electron energies).

Energy Resolution

In the past few years, a number of other materials that have been investigated have extremely promising properties, including La_3Br:Ce [13], La_3Cl:Ce [14], and $RbGd_2Br_7$:Ce [15]. These materials possess high luminous efficiency *with* excellent energy resolution and fast (~50 ns) decay time, but have relatively low density (~5 g/cc) and atomic number. Of these, La_3Br:Ce is probably the most promising material, with a light output of 61,000 photons/MeV (50% higher than NaI:Tl), a primary decay time of 35 ns (over 90% of the emitted photons are emitted with this decay lifetime), a density of 5.3 g/cc, and an emission wavelength of 360 nm [13]. One of the most spectacular aspect of this material is its energy resolution. It achieves 2.9% fwhm for 662 keV gamma rays — a resolution that is twice as good as that of NaI:Tl (which typically achieves 6% fwhm for this energy) and is comparable to many solid state detectors with comparable volume (~0.5 cc). A 662 keV photopeak observed in this material is shown in Figure 3. This material may have the potential to replace NaI:Tl as the material of choice for gamma cameras used for single-photon nuclear medical imaging techniques, such as SPECT.

Scintillation from Wide Band-Gap Semiconductors

Most inorganic scintillators used today are based on insulating host crystals in which luminescent ions or complexes are imbedded. Sometimes the luminescent centers are intrinsic, such as the cerium in CeF_3 or the tungstate complex in cadmium tungstate ($CdWO_4$), and sometimes they are dopants, such as the thallium in NaI:Tl or cerium in LSO. In these materials, the ionizing radiation initially forms holes in the valence band and electrons in the conduction band, with enough energy being transferred to the electron that it comes to rest many atomic diameters away from its original position. The holes are spatially localized (~1 atomic diameter in size) and diffuse to luminescent centers, placing the center in an ionized state. The ionized center than attracts an electron, placing the center in an electrically neutral but excited state, which then de-excites by radiating a scintillation photon. In many materials there are competing non-radiative de-excitation (*i.e.*, quenching) processes, mostly via competition for holes, which significantly reduce the light output.

The scintillation properties of these materials, notably the decay lifetime, are therefore heavily dependent on the luminescent center. The ideal luminescent ion would have a single, optically

active electron when it is in its preferred valence state (to prevent undesirable interactions between electrons), a spin / parity allowed transition (to achieve short decay lifetimes), and an ionic radius similar to that of high-Z ions (to allow doping in dense, high-Z host materials). Nature, however, has provided only a limited number of choices, and all have drawbacks. The ions that come closest to meeting these criteria are Ce^{3+} (which suffers from a small wave function overlap that increases its decay lifetime), Eu^{2+} (which prefers to be in the Eu^{3+} state, which yields spin / parity forbidden transitions), and Tl^{1+} (which is spin / parity forbidden). Thus, it is unlikely that scintillators based on insulators are likely to produce fast (sub nanosecond), luminous emissions.

This has re-kindled interest in a long-overlooked scintillation mechanism that is responsible for extremely fast (0.4 ns decay lifetime) and reasonably luminous (15,000 photons / MeV at room temperature) emissions in ZnO:Ga, as well as similar speed (but less luminous) emissions in CdS:In [16, 17]. It occurs in direct band-gap semiconductors — electrons in the conduction band recombine directly with holes in the valence band, resulting in near band-edge luminescence. These materials are covalently (rather than ionically) bonded, so the spatial extent of the hole includes many atoms. Therefore, the wavefunction of the hole is a mixture of many ionic wavefunctions and effectively mixes together the quantum numbers. This implies that the transitions will not be spin / parity forbidden and so will be fast, as long as they are direct (and so do not require phonons to participate in the transition).

Such ultra-fast luminescence has recently been observed in undoped CuI, HgI_2, and PbI_2, and plots showing the decay lifetime of these materials are displayed in Figure 4 [18]. These emissions are observed at cryogenic temperatures, but are quenched at room temperature. Similar behavior (sub-nanosecond emissions at cryogenic temperatures that are quenched at room temperature) is observed in undoped ZnO and CdS, but the addition of n-dopants (Ga and In respectively) increases the quenching temperature in these materials to the point where the room temperature emissions are reasonably luminous. There is hope that similar doping could make these newly discovered materials (CuI, HgI_2, and PbI_2) and other ssemicunductors bright, fast, scintillators at room temperature.

Conclusion

There has been a significant amount of recent progress in scintillators. New materials for high energy physics and positron emission tomography (lead tungstate and LSO, respectively) have recently completed the “development” phase of research and development and have just entered large scale production. There have been significant efforts to understand the fundamental limits of energy resolution in scintillators, and it recently has been shown that the energy-dependent nature of the proportionality factor between energy deposit and scintillation light can play a large

role. Several new scintillators that exhibit outstanding energy resolution have been discovered, and these show great promise for a variety of applications, notably nuclear medical imaging. Finally, there has been a re-kindled interest in scintillation in direct band-gap semiconductors, which have the potential to produce intense, sub-nanosecond emissions at room temperature.

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Figures

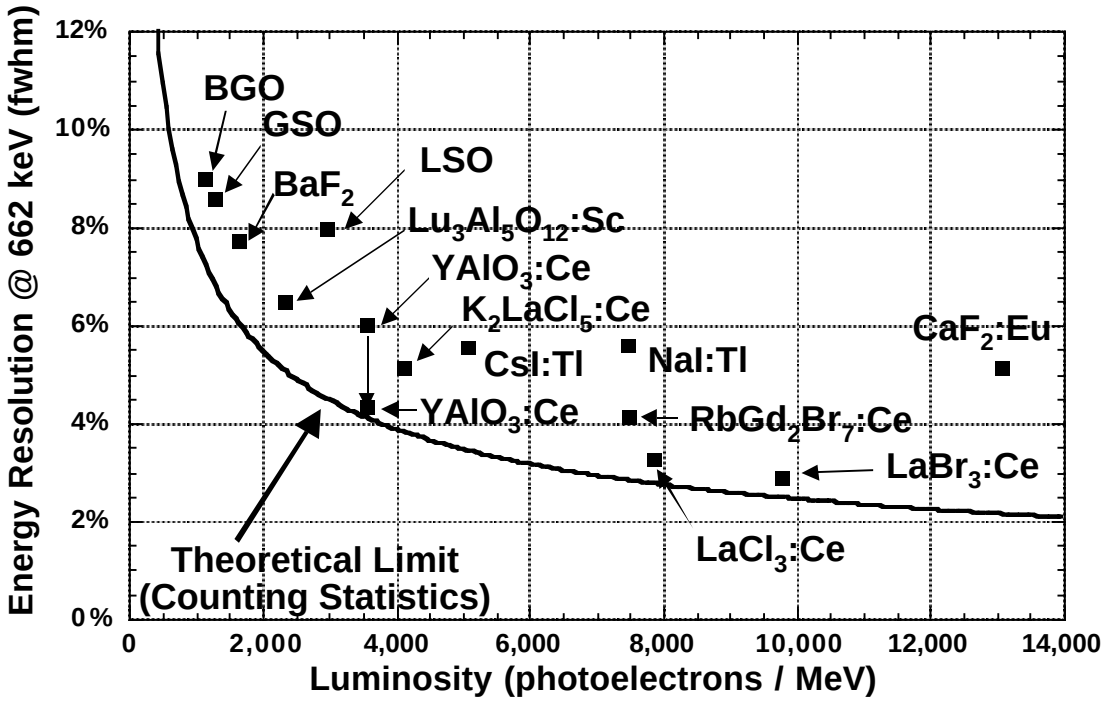

Figure 1: Measured energy resolution of several scintillators for 662 keV gamma rays as a function of their light output (expressed as the number of photoelectrons observed with a photomultiplier tube). The solid curve indicates the theoretical lower limit placed by counting statistics.

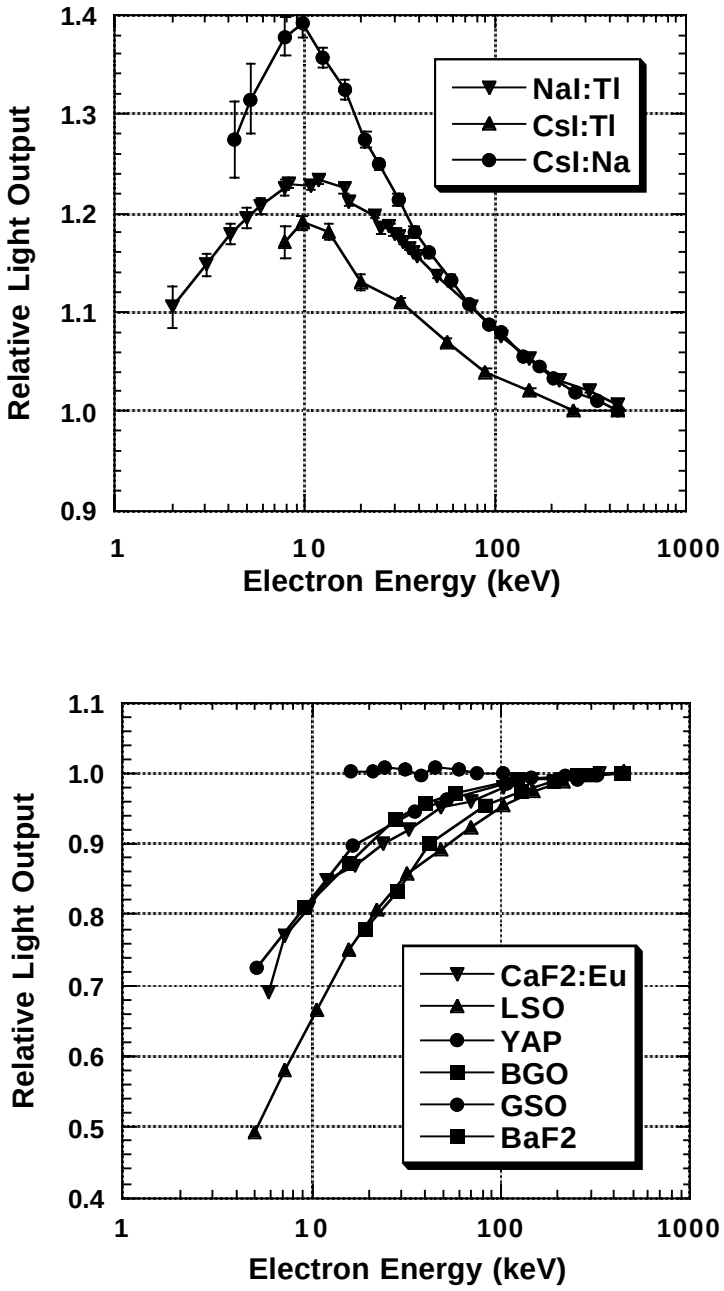

Figure 2: Electron energy response (relative light output, normalized to the value at 662 keV, as a function of electron energy) for various alkali halide (upper) and non- alkali halide (lower) scintillators. The response of an ideal material would be independent of electron energy.

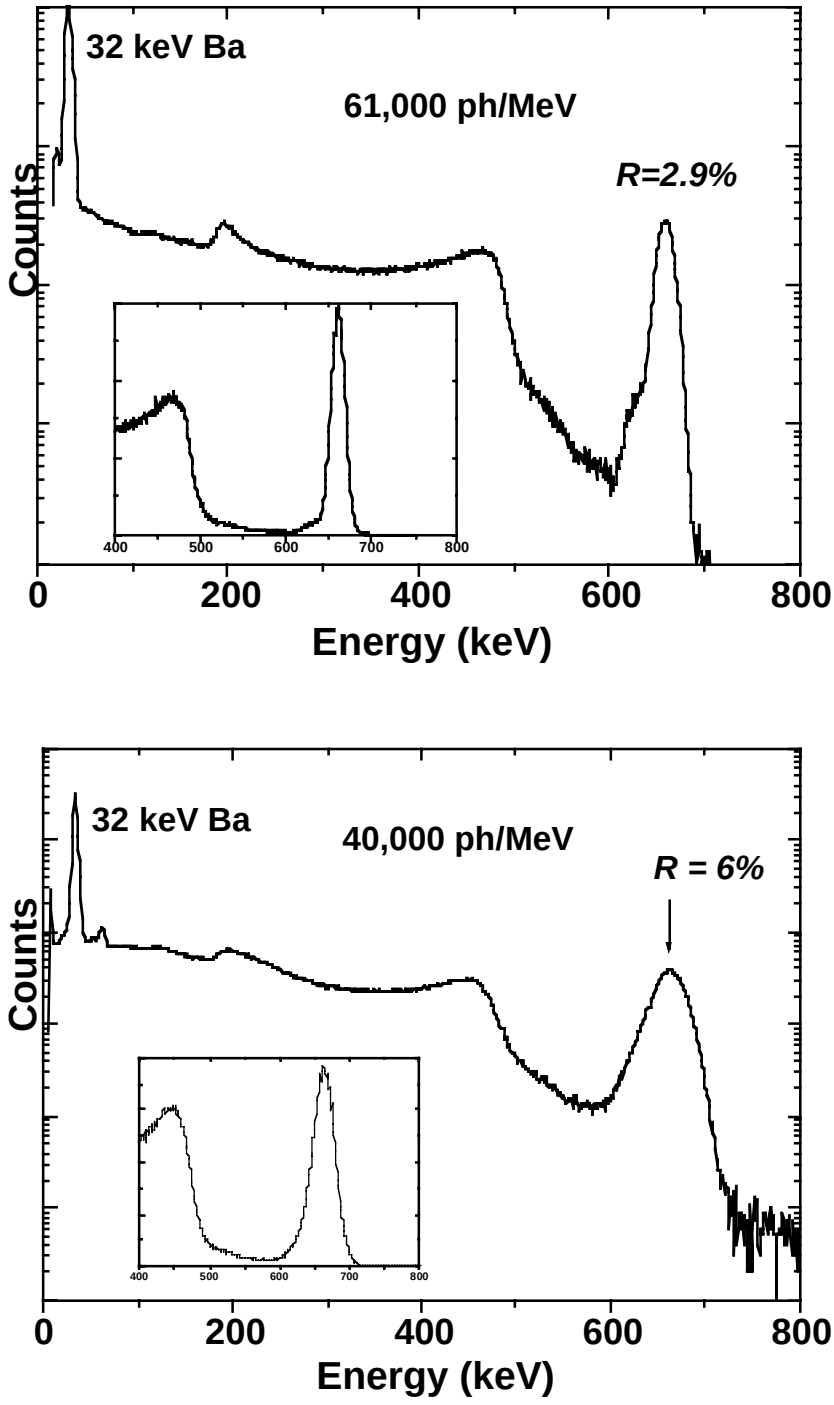

Figure 3: Pulse height spectra of LaB_{r3}:Ce (upper) and NaI:Tl (lower) when excited by 662 keV gamma rays. The ordinates are on a logarithmic scale — the inset plots show the same data on a linear scale.

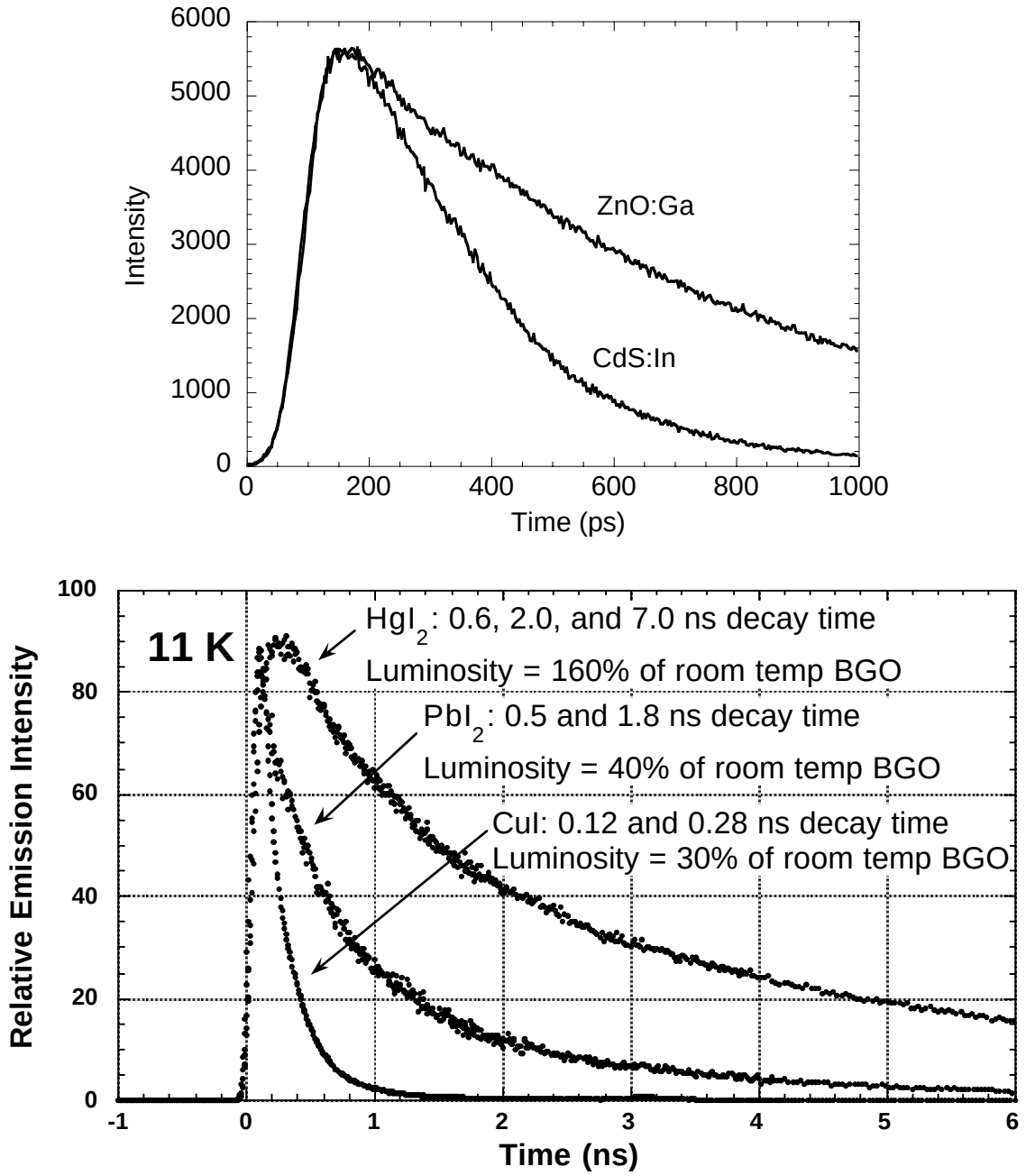

Figure 4: Decay time spectra at of several semiconductors that exhibit band-edge emissions, showing their extremely fast decay lifetimes. The upper plot show the room temperature emissions of ZnO:Ga and CdS:In, while the lower plot show the low temperature (11 K) emissions of undoped HgI_2, PbI_2, and CuI.