The quest for the ideal inorganic scintillator ☆

S.E. Derenzo*, M.J. Weber, E. Bourret-Courchesne, M.K. Klintenberg

Lawrence Berkeley National Laboratory, University of California, 1 Cyclotron Road, Mail stop 55-121, Berkeley, CA 94720, USA

Abstract

The past half century has witnessed the discovery of many new inorganic scintillator materials and numerous advances in our understanding of the basic physical processes governing the transformation of ionizing radiation into scintillation light. Whereas scintillators are available with a good combination of physical properties, none provides the desired combination of stopping power, light output, and decay time. A review of the numerous scintillation mechanisms of known inorganic scintillators reveals why none of them is both bright and fast. The mechanisms of radiative recombination in wide-band gap direct semiconductors, however, remain relatively unexploited for scintillators. We describe how suitably doped semiconductor scintillators could provide a combination of high light output, short decay time, and linearity of response that approach fundamental limits.
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1. History

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—is shown in Fig. 1. The discovery of scintillator materials may be divided into three periods. The first period included the earliest scintillators: $CaWO_4$ first used in the year following Röntgen's discovery of X-rays; uranyl salts used by Becquerel to discover radioactivity; and ZnS used by Crookes to detect and count radioactivity and by Rutherford to study alpha particle scattering [1].

The development of the photomultiplier tube in the 1940s and the discovery of scintillation in naphthalene led to a second period that began with Hofstadter's development of the thallium-activated NaI. In a burst of exploration during the following few years, the scintillation properties of most pure and activated alkali halide crystals were investigated [2]. Lithium containing compounds to detect neutrons and the first glass scintillators (activated with cerium) were also developed in the 1950s. In the ensuing decades a steady precession of new scintillator materials appeared including the discovery of fast core-valence luminescence in
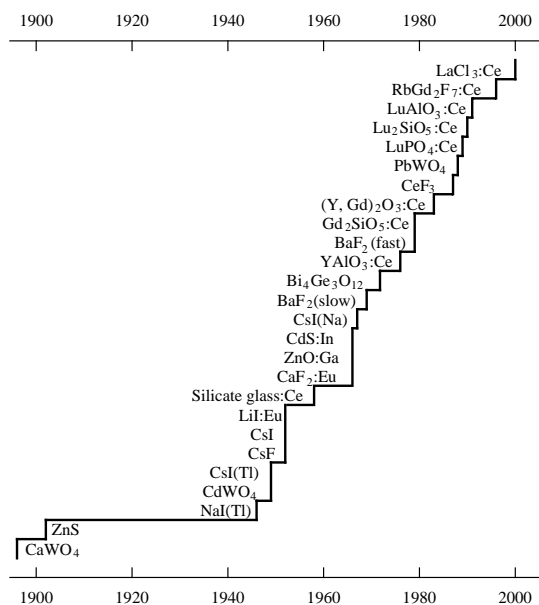
Fig. 1. History of the discovery of important inorganic scintillator materials.

BaF_2. A third period—the past two decades—has witnessed a veritable renaissance in research and development of scintillator materials, prompted in large part 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 furor of 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 [3]; the Materials Research Society Symposium on Scintillator and Phosphor Materials—San Francisco, 1994 [4]; and the biannual Inorganic Scintillators and their Applications conferences (SCINT 95—Delft [5], SCINT 97—Shanghai [6], SCINT 99—Moscow [7], SCINT 01—Chamonix [8]).

Concurrently with the discovery and development of materials, 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 for specific materials may still be lacking) [9–11].

2. Mechanisms in inorganic scintillators

Stage one: The ionization event creates an inner shell hole and an energetic primary electron, followed by radiative decay (secondary X-rays), nonradiative decay (Auger processes—secondary electrons), and inelastic electron–electron scattering in the time domain of $\sim 10^{-15}$–10^{-13} s. Typically it takes two to seven times the band gap energy of the crystal to create an electron–hole pair [12,13]. In some crystals the number of pairs created varies with recoil electron energy and this nonlinearity can limit the energy resolution for the detection of gamma rays by multi-step absorption.

Stage two: When the electron energy becomes less than the ionization threshold, hot electrons and holes thermalize by intraband transitions and electron–phonon relaxation. The charge carriers can remain as diffuse band states in the case of semiconductors, become trapped on defects and impurities, become self-trapped by the crystal lattice, or form free and impurity-bound excitons, all in a time scale of $\sim 10^{-12}$–10^{-11} s. During this stage luminescent centers may be excited by impact excitation by hot electrons, sequential electron–hole capture or sequential hole–electron capture, and sensitizer–activator energy transfer processes over a time scale ranging from $< 10^{-12}$ to $> 10^{-8}$ s. Depending on carrier mobility, this time is responsible for the intrinsic rise time of the scintillation light.

Stage three: The excited luminescent species return to the ground state by nonradiative quenching processes or by emitting a photon. The radiative process can be as short as 10^{-9} s for electron–hole recombination, free and bound exciton emission, and core-valence recombination, or can take many minutes for the case of highly forbidden processes.

There are many different luminescent species and scintillation mechanisms possible in inorganic

materials [14]. The luminescence may be intrinsic to the material and involve electron–hole recombination; free, self-trapped, and defect-trapped exciton luminescence; constituent transition group or post-transition group ion fluorescence; core-valence band transitions; or charge transfer transitions within a molecular complex. Or it may be extrinsic, such as luminescence associated with impurities or defects and additive dopant ions. In the role of an activator, the dopant ion may be the luminescence species or may promote luminescence as in the case of defect-bound exciton emission.

Examples of stage three luminescence are:

Free and impurity-bound exciton: Ionization electrons and holes can combine to form free excitons with electron–hole binding energies of a few to $\sim 60\,\mathrm{meV}$ [15]. At low temperatures these are usually bound as an entity to an impurity atom or defect with a binding energy of several meV. Radiative decay of free or bound excitons can be very fast ($<1\,\mathrm{ns}$), however at ambient temperatures the emission is weak because most excitons become unbound or disassociated.

Self-trapped exciton: In this case the ionization hole localizes on one or more atoms with associated lattice relaxation. The resulting Coulomb defect traps a spatially diffuse electron to create a self-trapped exciton [16]. The unpaired spin associated with the hole and the diffuse electron spin form a triplet state which has a radiative lifetime of typically $10^{-6}\,\mathrm{s}$ because the transition is spin forbidden. The singlet state decay can be much faster ($10^{-9}\,\mathrm{s}$), but is weaker. Examples of self-trapped excitons occur in NaI (pure), CsI(pure), and BaF_2. In the case of the halides, the self-trapped hole is commonly a V_k center consisting of a bound pair of halogen ions.

Self-activated scintillator: In these materials, the luminescent species is a constituent of the crystal. Emission involves intraionic transitions in the cases of Bi^{3+} in $Bi_4Ge_3O_{12}$ and Ce^{3+} in CeF_3 or charge transfer transitions in the case of $(WO_4)^{2-}$ in $CaWO_4$ and $CdWO_4$. In $Bi_4Ge_3O_{12}$ the ionization process results in a hole in the 6s level of Bi^{3+} and an excited electron in the 6p level. Since the hole is on a cation, these are also called cation excitons. The radiative $^3P_{0,1}-^1S_0$ transitions are

spin forbidden and slow at cryogenic temperatures. At room temperature both the decay time and the luminosity are reduced by competing nonradiative transitions.

Activator ions: For dopant ions such as Tl^+, Ce^{3+}, and Eu^{2+}, the ionization holes and electrons are sequentially trapped on the same luminescent ion. In several materials [e.g., CsI(Tl) and $LaCl_3$(Ce)] the luminosities can be very high, near the theoretical limit. For Ce^{3+} the electric-dipole 5d–4f transition is allowed, but is relatively slow (typically 20–40 ns) due to the poor spatial overlap between the 5d and 4f orbitals. The Eu^{2+} 5d–4f and Tl^+ $^3P_{0,1}-^1S_0$ decays are slower (about $1\,\mu s$) because the transitions are only partially spin allowed [14]. The rise time of the activator luminescence may be slow if one of the carriers has limited mobility as, for example, the slow hole migration in CsI(Tl) and NaI(Tl) [17,18].

Core-valence luminescence: In these materials (examples are BaF_2, CsF, RbF, $KMgF_3$, $BaLu_2F_8$) the energy gap between the valence band and the top core band is less than the fundamental band gap [19]. A photon is emitted when an electron in the valence band fills an ionization hole in the top core band. This is an allowed process and the decay time is of the order of 1 ns, however the luminosity is limited to about 2000 photons/MeV due to the inefficiency of creating holes in an upper core band.

As may be seen from the above, no commonly used scintillator is both bright and fast. The best present combinations of stopping power, speed, and luminosity are achieved in the recently developed Ce-activated scintillators.

3. Characteristics of an ideal scintillator

3.1. Physical characteristics

Detection efficiency: For gamma rays, stopping power is maximized by maximizing density and atomic number. High density and stopping power are important for reducing the amount of scintillator material needed. For neutron detection, a constituent ion with a high neutron absorption section such as ^6Li, ^{10}B, or ^{157}Gd is necessary.

Cost and physical form: These factors are closely related with the ease of crystal growth, because the cost of growing the crystal growth is usually much higher than the cost of the raw materials. Crystals that do not decompose or undergo a phase transformation between room temperature and their melting point are the easiest to produce in large shapes at low cost.

Chemical stability and mechanical strength: 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 are highly desirable characteristics.

3.2. Luminescent characteristics

Wavelength: The emission wavelength and the light yield will determine the best photodetector to use (e.g., photomultiplier tube, photodiode, avalanche photodiode).

Light yield: Whereas high light yield may not be too critical for detecting very energetic particles, for applications where the particle energy is smaller or fixed, e.g., in positron emission tomography, increased light yield is important for improving accuracy and spatial resolution. Energy resolution also depends on light yield and proportionality. CsI(Tl) has one of the highest light yields (65,000 photons/MeV).

Proportionality: If the average energy needed to create an electron–hole pair is proportional to the recoil electron energy, then monoenergetic gamma rays will produce the same number of electron-hole pairs (within statistics) no matter how many Compton interactions occur before the final photoelectric absorption. Deviations from this proportionality will result in a degraded energy resolution. LaBr$_3$(Ce) has a high light output (61,000 photons/MeV) and the best energy resolution for 662 keV gamma rays (2.9% FWHM) reported thus far [20].

Decay time: 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 afterglow is important in medical imaging.

Radiation hardness: Radiation damage, which may be irrelevant for detectors in many imaging applications, is extremely important for detectors in high-energy physics experiments.

Considering the above desired physical and luminescent characteristics, how well are they satisfied by semiconductors? Below we address the luminescence characteristics of semiconductors.

4. Wide band gap semiconductors

4.1. Ideal semiconductor

Consider a wide band gap (> 2 eV) semiconductor having a direct optical transition (electrons and holes recombine without a change in momentum). Whereas at low temperatures carriers combine to form free or impurity-bound excitons, at room temperature a thermal equilibrium of free excitons and separate electrons and holes would be expected. In the absence of native defects and impurities which act as nonradiative recombination centers, electrons and holes in a semiconductor remain spatially diffuse (i.e., do not self-trap by lattice relaxation). The excited state will therefore not be thermally quenched and the band-edge recombination radiation will be efficient (one photon per electron hole pair) and fast (ns) [15]. Little energy is lost by such band-edge emission in stage two above, in contrast to the case of activator luminescence where the electronic levels of the activator ion are in the gap.

4.2. Nonradiative recombination

Most semiconductors have native defects (vacancies, interstitials, antisites, dislocations, etc.) and contain impurity atoms, imperfections that are difficult to eliminate. These defects can form nonradiative recombination centers that promptly trap electrons and holes before they can recombine radiatively. If there is an energy barrier (activation energy) for trapping, the trapping will be reduced at cryogenic temperatures with a resulting increase in luminosity.

It is known from many examples of luminescent scintillators, such as CsI(Tl) and LaBr$_3$(Ce), that a small concentration of intentionally introduced activators can efficiently trap ionization holes and thereby compete with the nonradiative traps even at room temperature. Holes can also be trapped efficiently in semiconductors by suitable impurity atoms to prevent capture on nonradiative centers.

4.3. Donor–acceptor recombination

Semiconductors can have either donor levels or acceptor levels or both. In the last case there will be a statistical distribution of donor–acceptor pair (DAP) separations. This results in a distribution of DAP emission wavelengths and decay times. If the electrons and holes are trapped at random locations and thus are too far apart to recombine radiatively, the luminescence efficiency will be low.

As an example, consider the moderately dense semiconductor PbI$_2$, whose band gap is 2.5 eV. Near-band-edge emission is observed the ~ 500–530 nm region consists of exciton lines and broad bands shifted to lower energies which at attributed to donor–acceptor pair emission [21,22]. The scintillation exhibits a fast (ns), nonexponential decay with 1/e decay times at 10 K of 0.55, 2.4, 3.7, and 5.6 ns. The rise and decay rates of the broad bands decrease with increasing wavelength demonstrating that the recombination was associated with donor–acceptor pairs. The luminosity PbI$_2$ at 10 K is ~ 3000 photons/MeV. With increasing temperature the luminosity decreases much faster than the decay lifetime. Therefore, the reduction in luminosity is not due primarily to thermal quenching of the excited states but mostly to thermally activated trapping of charge carriers on nonradiative recombination centers [23]. If a pure perfect PbI$_2$ crystal were available, it would produce $\sim 200,000$ photons/MeV with a decay time of about 1 ns, characteristics that define ideal luminescent properties.

4.4. n-type and p-type semiconductors

In the 1960s, Willi Lehmann [24] explored the use of donor impurities in the direct semiconductor ZnO. The replacement of $\sim 0.3\%$ of the Zn atoms with Ga atoms introduces a degenerate donor band overlapping the bottom of the conduction band. The donor band electrons recombine with ionization holes resulting in a broad near-band-edge emission. Similarly, Lehmann found that In-doped CdS exhibited a featureless near-band-edge emission. The principal decay times of both materials are < 1 ns. The luminosities are low at room temperature but increase significantly at cryogenic temperatures. The decay times, however, remain fast [23]. These are examples of band to shallow acceptor trap recombination, but the defect that acts as a shallow hole trap was neither controlled nor understood [25,26].

Phosphorous-doped ZnTe is an analogous example of a p-type semiconductor exhibiting similar behavior where now ionization electrons combine with acceptor band holes.

4.5. Isoelectronic donors and acceptors

Nitrogen substituted for P in GaP is an example of an isoelectronic or isovalent center. Because N is more electronegative than P, nitrogen first attracts an electron, then it attracts a hole like an acceptor. Lattice relaxation results in the isoelectronic impurity behaving as a deep center.

Tellurium doped CdS is another example of an isoelectronic impurity where the less electronegative Te initially traps a hole followed by the capture of an electron and Stokes-shifted exciton emission that is strongly quenched above 200 K [27]. The scintillation properties of this material have been reported [28].

5. Codoping and band to trap radiative recombination

By using one foreign atom to provide a carrier band and another foreign atom to provide for efficient trapping of the other carrier, it should be possible to achieve a luminosity and decay time close to fundamental limits.

Figs. 2–4 show room-temperature pulsed X-ray measurements of powder samples of CdS doped with In, Te, and both In and Te. As discussed

above, CdS(In) has a donor band of electrons that radiatively recombine with ionization holes to produce near-band-edge emission at 520 nm with an initial exponential decay time of 0.2 ns (Fig. 2). CdS(Te) traps ionization holes on isoelectronic Te which radiatively combine with ionization electrons to produce a broad emission band centered at 640 nm with a nonexponential time spectrum that falls to e^{-1} in 13 ns, to e^{-2} in 40 ns, to e^{-3} in 75 ns, and to e^{-4} in 120 ns (Fig. 3). Codoped CdS(In,Te) traps ionization holes on Te atoms, and these recombine radiatively with electrons from the In donor band to produce a broad emission band almost identical to that of CdS(Te), but with an exponential decay time of 3.3 ns (Fig. 4). The wavelength spectrum of CdS(In,Te) closely resembles that of CdS(Te), demonstrating that the donor electrons combine with holes trapped on Te (Fig. 5). The luminosity of
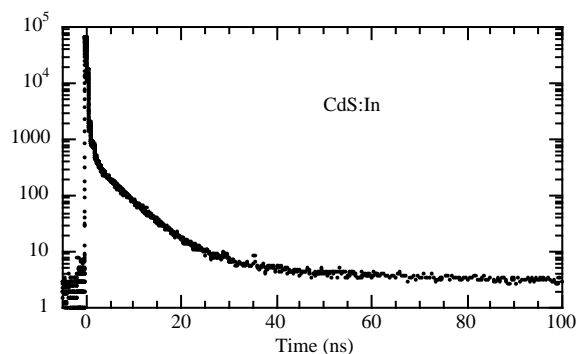

Fig. 2. Decay time spectrum of CdS doped with 1% In metal. The principal exponential decay time is 0.2 ns.
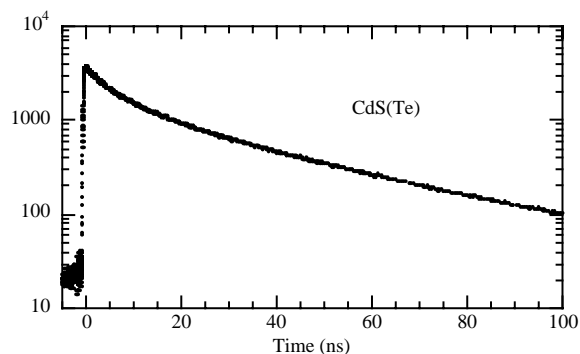

Fig. 3. Decay time spectrum of CdS doped with 0.01% CdTe.
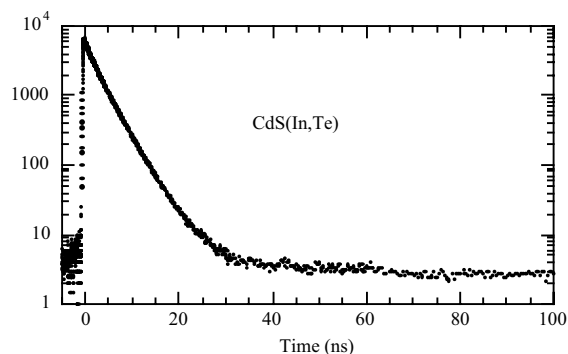

Fig. 4. Decay time spectrum of CdS doped with 0.5% In and 0.005% CdTe. Exponential decay time 3.3 ns.
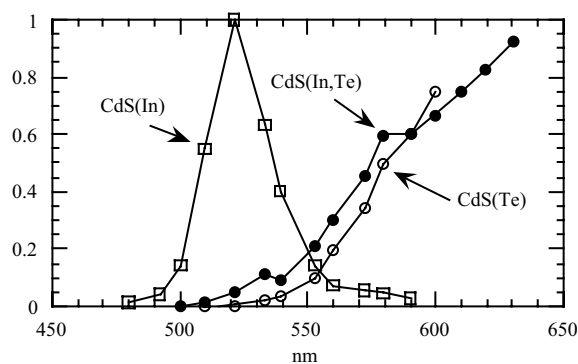

Fig. 5. Scintillation spectra recorded using 10-nm-bandpass interference filters showing that the emission of CdS(In,Te) is similar to that of CdS(Te). In contrast, the CdS(In) emission is a narrow band.

CdS(In,Te) increases strongly with decreasing temperature (similar to the behavior reported in Ref. [27]) and the decay becomes somewhat slower and nonexponential.

6. Discussion and summary

Several dozen useful scintillators have been developed over the past 50 yr, and these have involved a variety of scintillation mechanisms. In recent years Ce-activated insulator crystals have received considerable attention as scintillators. They take advantage of the relatively fast 5d–4f allowed transition and approach the maximum efficiency expected.

The use of semiconductors for scintillation is not new (as indicated in Fig. 1, ZnS was one of the earliest scintillators). We have found several semiconductor crystals that are fast and luminous scintillators at cryogenic temperatures. Useful room-temperature operation has been hampered, however, by carrier trapping on nonradiative recombination centers.

CdS(In,Te) is the first example of a class of fast room-temperature semiconductor scintillators in which ionization holes are trapped by added impurity atoms and then recombine radiatively with electrons provided by a donor band. Because the donor band provides electrons of both spin states, the radiative transition is spin allowed and fast.

Two promising areas of future research in the quest for the ideal scintillator are, first, the continued search for improved host crystals for Ce activation and, second, identification of dopants that would make wide band gap, direct, heavy semiconductors such as PbI_2 and HgI_2 fast and luminous at room temperature.

Acknowledgements

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