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Bright and ultra-fast scintillation from a semiconductor?

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ABSTRACT

Semiconductor scintillators are worth studying because they include both the highest luminosities and shortest decay times of all known scintillators. Moreover, many semiconductors have the heaviest stable elements (Tl, Hg, Pb, and Bi) as a major constituent and a high ion pair yield that is proportional to the energy deposited. We review the scintillation properties of semiconductors activated by native defects, isoelectronic impurities, donors and acceptors with special emphasis on those that have exceptionally high luminosities (e.g. ZnO:Zn; ZnS:Ag, Cl; CdS:Ag, Cl) and those that have ultra-fast decay times (e.g. ZnO:Ga; CdS:In). We discuss underlying mechanisms that are consistent with these properties and the possibilities for achieving (1) 200,000 photons/MeV and 1% fwhm energy resolution for 662 keV gamma rays, (2) ultra-fast (ns) decay times and coincident resolving times of 30 ps fwhm for time-of-flight positron emission tomography, and (3) both a high luminosity and an ultra-fast decay time from the same scintillator at cryogenic temperatures.

1. Introduction

A surprising variety of scintillation emissions have been observed from semiconductors, and most of them are quite different than those that occur in ionic crystals. Among the brightest is ZnS:Ag, Cl which produces so much scintillation light that alpha particles can be detected by the naked eye [1]. This also demonstrates that in semiconductors slow charged particles are almost as efficient in producing scintillation light as fast charged particles. Other semiconductor scintillators (e.g. ZnO:Ga, CdS:In [2]) have decay times in the 1 ns range, as short as core-valence scintillators (e.g. CsF [3,4], BaF_2 [5]) and the fastest organic scintillators (e.g. EJ-232, BC-422).

In Section 2 we summarize and compare the ionization processes that occur in semiconductors and ionic crystals. In Sections 3–7 we describe scintillation from semiconductors with native defects (Section 3), isoelectronic doping (Section 4), donor–acceptor complexes (Section 5), shallow (n-type) doping (Section 6), and cryogenic excitons (Section 7). Section 8 concludes with a review of the fundamental limits to the scintillation properties of semiconductors and possible approaches for designing compositions that approach those limits.

2. Ionization and excitation processes

During an ionization event in a crystal, electrons are ejected from their energy levels in the core and valence bands to higher levels in the conduction band. The missing electrons (holes) in the valence bands rapidly rise to the top of the uppermost valence band and the excited electrons rapidly drop to the bottom of the conduction band. Typically half of the deposited energy is converted to heat during this thermalization process. In a few crystals (e.g. CsF, BaF_2) the energy difference between an upper core band and the valence band is less than the band gap, resulting in an ultra-fast core-valence scintillation component.

In semiconductor crystals these charge carriers will be spatially diffuse until they recombine or are trapped on defects. Room temperature scintillation is based on doping with a combination of donor, acceptor, or isoelectronic impurities. At cryogenic temperatures (typically below 20 K) the charge carriers can remain spatially diffuse and combine to form free excitons or defect-trapped excitons. In direct-gap semiconductors this cryogenic scintillation can be bright and ultra-fast.

In pure ionic crystals it is energetically favorable for the hole to localize because the energy to be gained by lattice relaxation is greater than the energy required to localize the hole charge. The result is called a self-trapped hole that forms rapidly during thermalization. The self-trapped holes can attract ionization electrons to become self-trapped excitons that are usually quenched at room temperature [6,7]. 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} s because the transition is spin

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forbidden [8]. It is interesting that BaF_2 has both a core-valence emission and a useful self-trapped exciton emission at room temperature. In ionic crystals that contain a luminescent ion as a major constituent (e.g. $Bi_4Ge_3O_{12}$) the charge carriers combine to excite that ion. Alternatively, a native defect (vacancy, interstitial, antisite) can trap the carriers and become a exciton (e.g. ZnO:Zn). Most inorganic scintillators in common use are ionic crystals doped with a luminescent ion (e.g. Tl^{+}, Eu^{2+}, Ce^{3+}, and Pr^{3+}) that is excited by efficient trapping of the charge carriers. The luminescent ions Eu^{2+}, Ce^{3+}, Pr^{3+} have a single 4f electron in the ground state that is excited to the 5d level. The 5d–4f radiative transition is an allowed dipole transition but the decay times are limited by the poor spatial overlap between the d and f wavefunctions.

3. Bright scintillation from a semiconductor with a native defect

ZnO: Zn is an example of a bright scintillator where the emission center is a native defect. It is sold as a commercial phosphor (P15 or P24) and can be produced by adding approximately 100 ppm Zn metal to ZnO or by annealing ZnO in hydrogen to produce oxygen vacancies. The bright green emission is centered at 510 nm (2.43 eV), 0.94 eV less than the band gap of 3.37 eV. The decay time is several microseconds. Vanheusden et al. used EPR and PL measurements to determine that the emission mechanism was due to the radiative transition of an electron bound to the vacancy (i.e. a singly ionized oxygen vacancy) to a hole in the valence band produced by the excitation [9,10].

4. Scintillation from semiconductors with isoelectronic impurities

By replacing an element with another that has the same electronic structure states can be introduced into the gap. If the replacement is more electropositive (or electronegative) it can trap holes (or electrons) and be a center for radiative recombination with the other carrier [11].

4.1. *Semiconductors doped with isoelectronic hole traps*

CdS:Te and ZnSe:Te are examples of commercially available scintillators that use tellurium as an isoelectronic hole trap [12,13]. Sulfur and selenium have very similar electronegativities (2.58 and 2.55 eV, respectively). Tellurium has an electronegativity of 2.1 eV and acts as a hole trap when it replaces one of the former.

CdS:Te has a broad emission spectrum with a maximum at 640 nm (1.94 eV), 0.55 eV from the 2.49 eV band edge and the main decay components are 270 ns and 3.0 μs [14]. At room temperature configurational thermal quenching reduces the luminosity [15].

4.2. *Semiconductors doped with isoelectronic electron traps*

ZnSe:O and ZnTe:O are examples of scintillators with an isoelectronic impurity that traps electrons.

ZnSe:O is a scintillator with a peak emission wavelength of 595 nm (2.08 eV), 0.62 eV less than the band gap of 2.70 eV [16]. Its scintillation luminosity is 1.28 times that of CsI:Tl and there are two decay times of 4 μs and 12 μs [17]. A small crystal exhibited a pulse height resolution of 7.4% fwhm for 662 keV gamma rays [17].

ZnTe:O is a scintillator with a peak emission wavelength at 680 nm (1.82 eV), 0.44 eV below the band gap of 2.26 eV [18–20]. Our calculations show that oxygen on a tellurium site introduces an empty donor state about 0.4 eV below the conduction band minimum. Ionization electrons trap on those donor sites and then attract ionization holes to form excitons that have long decay times.

5. Bright scintillation from semiconductors with donor–acceptor complexes

ZnS:Ag, Cl is a commercial phosphor (P11) with an emission peak at 450 nm (2.76 eV), 0.78 eV from the band edge at 3.54 eV. Many combinations of dopants and codopants have been reported, but the highest luminosity is achieved by using Ag (an acceptor) as the primary dopant and Cl (a donor) as the codopant. It is a well-studied phosphor and the high luminosity is attributed to a donor–acceptor complex that is very efficient in trapping ionization electrons and holes [21–25]. Our measurements show that 1) the rise time is sub-ns, 2) the decay is complex with components as long as 100 μs, and 3) the luminosity is about six times higher than $YAlO_3$:Ce phosphor powder. In spite of the rapid and efficient production of the excited states, the donor electron/acceptor hole spatial overlap is poor and the decay time is long.

CdS:Ag, Cl is a similar phosphor with a high luminosity and an emission peak at 620 nm (2.0 eV), 0.5 eV from the band edge at 2.5 eV [26]. CdS:Ag, Cl can be blended with ZnS:Ag, Cl in any ratio to adjust the emission wavelength from 450 to 620 nm. We have found that the rise and decay times are similar to those of ZnS (Ag, Cl).

6. Ultra-fast scintillation from semiconductors with shallow (n-type) donor impurities

6.1. *n-type ZnO*

ZnO:Ga has been long known as an ultra-fast near-band-edge scintillator [2,27]. The gallium donor ion on a zinc site is charge compensated with electrons whose energy is close to the bottom of the conduction band. Above the Mott critical density of about $7 \times 10^{19}\ \mathrm{cm}^{-3}$ (0.17%) the donor electrons from a conducting band as their wavefunctions overlap [28,29]. The highest luminosity of ZnO:Ga occurs at gallium concentrations above 0.05% and when hydrogen is used in the synthesis, which is consistent with the notion that H^{+} acts as a hole-trapping acceptor and radiative center (e.g. ZnO:Ga, H) [30,31]. ZnO:Sc has also been found to be an ultra-fast scintillator [32].

6.2. *n-type CdS*

CdS:In is an ultra-fast near-band-edge scintillator where indium is the donor ion [2,33]. When indium is used to provide donor electrons and tellurium is used as an isoelectronic hole trap (CdS:In, Te), fast emission occurs near the emission wavelength of CdS:Te with a decay time of 3.3 ns [34,35]. This shows that delocalized electrons that are not in a definite spin state relative to the tellurium-bound hole can increase the radiative recombination rate by more than 100-fold.

7. Scintillation from semiconductors at cryogenic temperatures

In this section we describe semiconductors at cryogenic temperatures. Semiconductors have an advantage over ionic crystals in that ionization holes do not spontaneously self-trap by lattice deformation [6,7] but can bind with ionization electrons to form