Role of excitons in the energy resolution of scintillators used for medical imaging

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Abstract. Theoretical investigations suggest that the nonproportionality in a scintillator is caused by the high excitation density created within the track of an X-ray or γ ray photon entering in a scintillating crystal. In this paper an analytical expression for the scintillator yield is derived. For the case of BaF$_2$ scintillator the role of excitons created within the γ-ray track in the scintillator yield is studied. By comparing the results of two theories an analytical expression is also derived for an energy parameter which could otherwise only be determined by fitting the theoretical yield to the experimental data.

1. Introduction

The world today needs scintillators that have better energy resolution for improving diagnostic accuracy in medical imaging and identification of contraband nuclear materials in homeland and global security. Existing scintillators have poor energy resolution. Hence there is huge demand for inventing new scintillators with superior energy resolution for better human health and security. This is due to the fact that nuclear medical imaging systems, like the single photon emission computed tomography (SPECT) diseases and positron emission tomography (PET) are envisaged to be the most popular diagnostic systems of human health because they have faster patient throughput, greater patient comfort, diagnostic certainty and staging accuracy. This enables practitioners better treatment planning of diseases like cancers, tumours, heart diseases and Alzheimer’s. In addition there are more than 49,000 airports and 926 seaports at present in the world which require detectors of contraband nuclear materials at each of their entrances for their country’s border and homeland security. Each of these detecting systems also requires, now more than ever, scintillators with superior energy resolution.

A γ photon absorbed in a scintillator first creates a pair of very high energy electron (e) and hole (h) which relaxes in a cascade process and creates many secondary e-h pairs with energies close to the band gap; some of them recombine radiatively and some non-radiatively. The photons emitted due to the radiative recombination contribute to the light yield of a scintillator and is defined as the integrated light output per MeV of energy deposited in a scintillator. The light yield is not constant with the incident γ energy, typically in the range of 10 keV to 1 MeV, in most scintillators which is referred to as nonproportionality or nonlinearity [1-2] and it seriously affects their attainable energy resolution leading to poor quality and inaccurate imaging. A few theoretical attempts [3-4] have recently been made in
understanding the nonproportionality in inorganic scintillators and accordingly it has been revealed that it is caused by the high excitation density created within the track of an X-ray or a γ-ray photon entering in a scintillating crystal. In this paper, following our recent approach [4] the light yield is first derived as a function of the excitation density created within the track of a γ-photon. Then using the excitation density as derived by Jaffe [3], the yield is derived as a function of the total deposited energy. Finally the results are compared with those in [3].

2. Theoretical developments

Following [4] we consider a cylindrical γ-ray track of radius \( r \) in a scintillating crystal and only excitons and pairs of electron and hole (e-h pairs) are generated in the track. Phonons are of course generated in relaxation of energetic carriers and self-trapping of excitons. The dynamical changes in exciton and e-h pair densities at any point, \( x \), along the track can be expressed by the following two rate equations [4]:

\[
\frac{dn_{ex}(x)}{dt} = (R_{1x} + K_{1x})n_{ex}(x) + (R_{2x} + K_{2x})n_{ex}^2(x) - \gamma_{ex}n_{eh}(x) + \gamma_{xe}n_{ex}(x) + K_{3x}n_{ex}(x)^3 - f_x n(x) \delta(t),
\]

(1)

\[
\frac{dn_{eh}(x)}{dt} = (R_{1eh} + K_{1eh})n_{eh}(x) + (R_{2eh} + K_{2eh})n_{eh}^2(x) - \gamma_{xe}n_{ex}(x) - \gamma_{ex}n_{eh}(x) + K_{3eh}n_{eh}^3(x) - (1 - f_x) n(x) \delta(t),
\]

(2)

where \( n_{ex}(x) \) is the excitonic concentration and \( n_{eh}(x) \) is the concentration of excited e-h pairs not bound like excitons at any point \( x \) on the track. \( f_x \) is the fraction concentration of excitons, \( 1 - f_x \) is the fraction concentration of e-h pairs, and \( n(x) \delta(t) \) represents the total number of excitations, \( n(x) = n_{ex}(x) + n_{eh}(x) \), created by the incident energy at time \( t = 0 \) at any point \( x \) along the track. Accordingly, \( n(x) \) (cm\(^{-3}\)) is defined as:

\[
n(x) = \left( -\frac{\partial E}{\partial x} \right) \frac{\pi r^2}{E_{eh}},
\]

(3)

where \( E \) is the total initial energy incident at any point \( x \), \( \pi r^2 \) is the average area of cross section of the track and \( E_{eh} \) is the average energy required to create an excitation in a scintillator, and here it is assumed to be three times the band gap energy \( (E_g) : E_{eh} = 3E_g \).

The validity of the concept of average radius has been addressed in [4].
In equations (1) and (2), $R_i$ and $K_i$ denote the rates of radiative and non-radiative (quenching) recombination of excitons, respectively, and $i = 1, 2$, denote through linear (1) and binary (2) processes. $R_{leh}$ and $K_{leh}$ ($i = 1, 2$) are the corresponding rates of recombination for an e-h pair, and $K_{3x}$ and $K_{3eh}$ are rates of non-radiative Auger (ternary) recombination of excitons and an e-h pairs, respectively. It is assumed here that Auger processes do not contribute to any radiative recombination. $\gamma_{ex}$ and $\gamma_{xe}$ are rates of converting an e-h pair into an exciton and vice versa, respectively. It is important to consider both the possibilities for applying the theory at higher temperatures. According to Eqs. (1) and (2), we can classify scintillators in three categories: (i) excitonic with $f(x) = 1$, (ii) non-excitonic with $f(x) = 0$, and (iii) mixed case $0 < f(x) < 1$.

In the track all the radiative channels contribute to the emission of photons which are detected and hence the light yield or scintillator yield is defined as the total emitted photons divided by the total excitations created in the track. In this way following [4] the scintillator yield is obtained as (details of derivation are given in [4]):

$$Y = \frac{a_1 n + a_2 n^2}{a_3 n + a_4 n^2 + a_5 n^3},$$

where $n$ is the total number of excitations created in the track and using the Bethe expression for the stopping power [5] and following Jaffe [3] it is approximately obtained as:

$$n \approx \left[ \frac{20e^4 \kappa^2 N_e}{E_{eh} r^2} \right] E^{-1},$$

where $e$ is the electronic charge, $\kappa = (4\pi\varepsilon_0)^{-1} = 8.9877\times10^9$, $N_e \approx 10^{30}$ m$^{-3}$ is the density of ground-state electrons in the track and $E$ is the total energy deposited in the track. Following [4] the other quantities appearing in the yield equation are defined as:

$$a_1 = R_{1x} A + R_{leh} B$$

$$A = \frac{[\gamma_{ex} + (R_{leh} + K_{1eh}) f_x]}{(R_{1x} + K_{1x})(R_{leh} + K_{1eh}) + \gamma_{ex}(R_{1x} + K_{1x}) + \gamma_{xe}(R_{leh} + K_{1eh})}$$

$$B = \frac{[(1 - f_x)(R_{1x} + K_{1x}) + \gamma_{xe}]}{(R_{1x} + K_{1x})(R_{leh} + K_{1eh}) + \gamma_{ex}(R_{1x} + K_{1x}) + \gamma_{xe}(R_{leh} + K_{1eh})}$$

$$a_2 = \frac{R_{2x} A^2}{2\tau_x} + \frac{R_{2eh} B^2}{2\tau_{eh}}; \quad \tau_x^{-1} = R_{1x} + K_{1x} \text{ and } \tau_{eh}^{-1} = R_{leh} + K_{1eh}$$

$$a_3 = (R_{1x} + K_{1x}) A + (R_{leh} + K_{1eh}) B$$
Using Eq. (5) the yield in Eq. (4) can be written as:

\[ Y = \frac{a_1 Q E^{-1} + a_2 Q^2 E^{-2}}{a_3 Q E^{-1} + a_4 Q^2 E^{-2} + a_5 Q^3 E^{-3}} \]  

(7)

where \[ Q = \frac{20 e^4 \kappa^2 N_e}{E_{eh} r^2} \]  

(8)

The yield obtained in equation (7) is of a similar form as obtained in [3] except that it takes into account up to third order processes. In [3] only two, one radiative and one non-radiative, processes are considered. The details of yield in equation (7) and associated analysis will be published elsewhere. Here onward we also consider only two channels so that the results can be compared with the previous theory [3]. We ignore the second order radiative and third order non-radiative processes, which means that neglect \( a_2 \) and \( a_5 \). This does not affect to any aspect of the mathematical formalism because the actual yield derivation is based on only first order processes [4]. Thus the yield in equation (7) can be expressed as:

\[ Y = \frac{a_1 E^p}{a_3 E^p + E^q K^{p+q}} ; \quad K = \frac{a_4}{a_3} Q \]  

(9)

where \( p = -1 \) and \( q = -2 \). Except for the factor \( a_1 / a_3 \), the yield in equation (9) is the same as obtained in [3] by Jaffe, however here the energy parameter \( K \) is not really a parameter but it is a function of the rates of radiative and non-radiative processes as it can be seen from equations (6) and (9). In [3] \( K \) has been determined by fitting the yield to the experimental data.

Experimentally the scintillator yield is calculated, as a customary or convention, in relation to the yield at \( E = 662 \text{ keV} \). Here also if we divide the yield in equation (9) by its value at \( E = 662 \text{ keV} \), we get an expression for the relative yield \( Y_R \) identical to that obtained in [3] as:

\[ Y_R = \frac{Y}{Y_{662}} = \left( \frac{662 \text{ keV})^\alpha + K^{-\alpha}}{E^{-\alpha} + K^{-\alpha}} \right) \]  

(10)

where \( \alpha = p - q \). For \( p = -1 \) and \( q = -2 \), \( \alpha = 1 \). It is to be noted that in the relative yield \( Y_R \) in equation (10) the factor \( a_1 / a_3 \) plays no role. This is based on the assumption that rates of radiative and non-radiative processes are independent of the incident energy, which is a reasonable assumption. In this approach the energy \( K \) can be calculated from equation (9) if the required radiative and non-radiative rates in equation (6) are known. This will be carried
out in the next section. The important point is that the energy $K$ is a function of the track radius, average energy of excitation and the rates of radiative and non-radiative processes. Therefore $K$ comes out as the most important quantity in the yield that contains all information about the track as well as all the processes taking place within the track.

3. Results

The important aspect of this paper is that one can calculate $K$ theoretically from equation (9) and verify that it agrees or not with that obtained by fitting equation (10) to the experimental yields measured in some scintillators. Jaffe [3] has carried out a very comprehensive task of fitting equation (10) to the experimental data for seven scintillators, namely CsI, CaF$_2$:Eu, GSO:Ce; K$_2$LaCl$_5$:Ce; Lu$_2$SiO$_5$:Ce, BaF$_2$ and RbGd$_2$Br$_7$:Ce, and thus determined $\alpha$ and $K$. We have also calculated the yield for four scintillators, namely NaI:Tl, BaF$_2$, GSO:Ce and LaCl$_3$:Ce, in [4]. The common scintillators studied in [3] and [4] are BaF$_2$ and GSO:Ce. We will focus only on BaF$_2$ scintillator in this paper for comparison but a more comprehensive analysis involving other scintillators will be published elsewhere.

According to [4], BaF$_2$ is an excitonic scintillator which means that dominantly the created electron and holes form excitons. In this case $f_x = 1$ which gives $K$ from equation (9) as [4]:

$$K = \frac{Q(R_{2x} + K_{2x})}{2(R_{1x} + K_{1x})}$$  \hspace{1cm} (11)

For BaF$_2$ according to [4], $R_{1x} = 1.6 \times 10^9$ s$^{-1}$, $K_{1x} = 4 \times 10^8$ s$^{-1}$, $R_{2x} = 0$ and $K_{2x} = 2 \times 10^{-17}$ m$^3$s$^{-1}$. Taking $r = 2$ nm [4] and $E_{eh} = 15$ eV [3], we get $Q = 6.8931 \times 10^9$ eV/m$^3$ and then from equation (11) we get $K = 3.44$ keV. This is in fair agreement with 4.28 keV obtained by Jaffe [3] from fitting equation (10) to the experimental data. It also agrees quite well with the average value of 3 keV obtained in [3] for seven scintillators. This clearly demonstrates the significant role that rates of radiative and non-radiative processes play within the $\gamma$-ray track in a scintillator. The details of the yields in equations (7) and (10), including other scintillators, will be published elsewhere.

4. Discussions

The scintillator yield derived earlier in [4] following an analytical and phenomenological approach is used to evaluate the yield for a special case considered in [3], where only two processes, one radiative and other non-radiative, are considered to occur within the track of a $\gamma$-ray photon entering a scintillator. By comparing the analytical yield derived here in equation (10) with that obtained in parametric form one gets an analytical form of the parameter. This is a very distinct advantage of this comparative method because the parameter $K$ in equation (10) could only be determined earlier by fitting equation (10) to the experimental data. Now $K$ can be calculated without fitting if the rates and track parameters are known. The calculated $K$ here agrees quite well with its fitted value for BaF$_2$ scintillator. A detailed comparison for other scintillators, including the third order process through equation (7) will be carried out in future and published elsewhere.

It may be noted that here we have the value of $\alpha = 1$ in equation (10), which however varies for different scintillators in [3]. For example, for BaF$_2$ $\alpha = 1.4$ and for CsI it is 1.29, etc. This may be attributed to the fact that Jaffe [3] has considered only two processes that quench excited carriers in the track, a radiative of order $p$ and a non-radiative of order $q$ without specifying $p$ and $q$. This is different from the present approach in equation (7) where...
three orders of processes are considered specifically and as the yield in equation (10) is a special case of equation (7) by neglecting the third order process, here $p = -1$ and $q = -2$. As the experimental data are representative of all processes occurring within the track, by fitting these only two processes, one is expected to get a value for $\alpha$ different from 1.

Here we have considered only the excitonic scintillator with $f_x = 1$. Apparently all the cases considered in [3] are close to this case; most are excitonic scintillators. The classic scintillator of sodium iodide doped with thallium (NaI:Tl) shows a different scintillator yield. In this case $f_x << 1$ [4]. The observed characteristics of the light yield show a rise with decreasing energy from the highest energy. Then a maximum occurs in the middle energy range which decreases again as energy decreases to the lower values. This feature of the yield in NaI:Tl or intrinsic NaI scintillators cannot be obtained by fitting data only to two processes. It is of course very desirable to study the yield in other well known scintillators used in SPECT and PET medical imaging systems, e.g., LYSO and YAP. However, here we present only some initial developments in the study of nonproportionality and as stated above a more comprehensive study will be published elsewhere.

5. Conclusions
An analytical expression for the scintillator yield is derived as a function of the $\gamma$-ray incident energy by incorporating the rates of first, second and third order processes. By comparing the yield derived in [3] and [4] an analytical expression is also obtained for the energy parameter $K$ which could otherwise be determined only by fitting the yield in equation (10) to the experimental data.

References
[1] Dorenbos P, de Haas J T M and van Eijk C W E 1995 IEEE Trans. Nucl. Sci. NS-42 2190
[2] Moszynski M, Zalipska J, Balcerzyk M, Kapusta M, Mengesha W and Valentine J D 2002 Nucl. Instr. And Meth. A 484 259
[3] Jaffe J E 2007 Nucl. Instr. And Meth. In Phys. Res. A 580 1378
[4] Bizarri G E, Moses W W, Singh J, Vasile’v A N and Williams R T 2009 J. Appl. Phys. 105 044507
[5] Bethe H A 1939 Ann. Phys. 5 325