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Recombination and scintillation processes in $YAlO_3$:Ce

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Abstract. This paper reports spectroscopic and scintillation studies of the well established scintillator material $YAlO_3$:Ce. Standard measurements of luminescence emission and excitation spectra have been accompanied by investigations of thermoluminescence and scintillation light yield over a wide temperature range, and by decay measurements under pulsed gamma and VUV excitations at various temperatures. These measurements are interpreted in the framework of a model that includes a recombination centre (Ce^{3+}) and a number of electron traps. We demonstrate that some unusual and largely unexplained features of the $YAlO_3$:Ce scintillator, such as a substantial disparity between scintillation and radiative decay times, the presence of slow components in scintillation decays, and a strong temperature variation of scintillation light yield between 150 and 300 K, have their origin in the processes of charge carrier capture and emission by electron traps. Although the nature of these traps remains elusive, most of the trap parameters, such as frequency factors, energy depths, and relative populations, have been estimated. This makes it possible to predict the characteristics of trap-free material and thereby the potential improvements that could be achieved.

1. Introduction

Yttrium orthoaluminate ($YAlO_3$, commonly known as yttrium aluminium perovskite, or YAP) is a particularly versatile luminescent material, with such diverse applications as solid-state lasers (YAP:Nd) [1, 2], cathode-ray detectors [3] and scintillators (YAP:Ce and YAP:Pr) [4, 5]. YAP:Ce in particular has many attractive properties, such as reasonably high density, fast decay, negligible afterglow, high light yield, and very good energy resolution [6]. These have made it a material of choice for many devices [7], including a small animal PET camera [8], a prototype gamma camera based on a position sensitive photomultiplier tube (high resolution single photon emission computed tomography or HIRESPECT) [9, 10], dosimeters [11], scintimammography cameras [12], and pulse-shape discrimination for the Astro-E Hard X-ray Detector [13]. Consequently, significant efforts have been put into technological development of the material [14, 15], as well as characterization of its optical [16–18] and scintillation properties [19–22].

These measurements reveal an interesting discrepancy. Optical excitation into the Ce^{3+} absorption bands yields reported values of the Ce^{3+} fluorescence decay time falling in a narrow range of 16–18 ns [16, 17, 23]. In contrast, reported values of scintillation decay

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times span a much wider range of 25–38 ns [14, 19, 24], with a distinct dependence on Ce content. Despite the relatively large differences between radiative and scintillation decay times, however, both of them remain very nearly single exponential in nature. To our knowledge this peculiar and important feature of the YAP:Ce scintillator, although well known and reported by many researchers, has remained unexplored and unexplained. To fill this gap is one of the motivations of the present work.

In elucidating this peculiar kinetic behaviour, one of our major tools will be the phenomenon of thermoluminescence. Such measurements are not routinely performed on scintillator materials, except for the study of radiation damage, and are usually made at temperatures well above 300 K, which we term high-temperature thermoluminescence or htTL. It is commonly accepted that good scintillator materials do not (and should not) produce a large TL output [25], a point of view confirmed by a recent study of YAP:Ce and its close relative, $LuAlO_3$:Ce (LuAP:Ce), by Bartram *et al* [26]. These workers directly measured the loss of scintillation light output at 300 K in both materials attributable to traps that glow above that temperature, finding values of 2% and 12%, respectively. The clear correlation between greater light output and lower htTL of YAP:Ce provides quantifiable evidence of the importance of electron traps as a source of loss in scintillation light yield.

Measurements of how the scintillation yield varies with temperature can shed even more light on this relationship. Since such measurements are typically utilized only for the restricted goal of evaluating the temperature stability of the output, they have generally been performed over a relatively narrow range of temperatures around ambient (290–300 K) [21]. For YAP:Ce, however, Korzhik *et al* [20] have measured the scintillation light output over a much wider temperature range of 100–600 K. Unfortunately, these authors note only that the light yield curve flattens at about 300 K and remains that way up to 500 K, and point to applications that would benefit from such a thermally stable yield. The enormous change of the YAP:Ce scintillation yield below 300 K (almost a fourfold increase from the cryogenic level) remained unexplored, presumably because it was felt to be irrelevant to the practical (room-temperature) performance of the material.

It turns out, however, to be quite relevant indeed. In two recent papers, Wojtowicz *et al* [27, 28] report measurements of htTL in LuAP:Ce and YAP:Ce combined with measurements of scintillation light yield over a temperature range 100–400 K. Results of both experiments were interpreted in the framework of a simple kinetic model with one trap and one recombination centre. They conclude that traps are in fact responsible for the observed strong scintillation light yield dependence on temperature, but these traps *are not* the ones that produce the glow peaks above 300 K observed in htTL experiments. On the contrary, the model indicates that the traps relevant to the large thermal variations of the light yield must be shallower, exhibiting glow peaks at temperatures below 200 K. Moreover, these results indicate that the loss attributable to traps can be even more severe than was revealed by the quasi-steady state measurements performed by Bartram *et al* [26]. Low-temperature thermoluminescence (ltTL) has much to tell us about both the light output and kinetic behaviour of scintillator materials.

In this paper we present results of measurements of the scintillation light yield, scintillation decays, and, most importantly, thermoluminescence over the critical temperature range below 300 K on the YAP:Ce scintillator material. These experiments were designed to explore some peculiar features of the scintillation behaviour of YAP:Ce, such as the slower than radiative decay at room temperature and the large thermal variations of the light yield. As will shortly become evident, all these features can be consistently explained in terms of the presence of relatively shallow traps which interfere with the radiative recombination of charge carriers via Ce^{3+} ions.

2. Experimental details

The $YAlO_3$:Ce crystal investigated in this work was grown by pulling from the melt by means of the Czochralski method. Individual specimens, with typical dimensions of $0.5 \times 0.5 \times 0.1$ cm^3, were cut from the larger boule and polished before measurement. The Ce content of the material, as ascertained by means of mass spectroscopy, fell in the range 3000–4300 ppm by weight.

ltTL glow curves were measured using a McPherson VUV excitation-emission spectrometric apparatus, equipped with a closed-cycle helium cooler controlled by a programmable heater. Irradiation was performed with a deuterium lamp through a 0.2 m monochromator with a 1200 lines/mm grating, and the TL emission was measured by means of a 0.35 m monochromator with a 2400 lines/mm grating set at zero order. Specimens were placed within an evacuated sample chamber situated between the two monochromators. Thermoluminescence measurements were performed in a range of 15–300 K at a linear heating rate of 0.15 K s^{-1}. Signal detection was performed by the photon counting method, and data acquisition was fully computerized.

Scintillation light yield measurements were made using a set-up with a sample chamber designed to accommodate a radioactive source (^{137}Cs, 10 μCi) and to maximize the collection of scintillation light. The YAP:Ce samples were excited by γ-photons from the source at various temperatures in the range 90–400 K. The light generated in each individual scintillation event during the appropriate time window (between 0.5 and 12 μs) was converted into a proportional voltage pulse, which was digitized and counted by a multichannel analyser. In such a configuration each channel contained the number of events in which a given quantity of photons was detected, allowing the light yield to be expressed as the location of the photopeak, i.e. the quantity of photons emitted by those events in which the full energy of the gamma was deposited in the crystal.

Scintillation time profile measurements, based on the well known standard method of synchronous photon counting [29], were performed on the same set-up as the scintillation light yield measurements. In this case, however, the detection system was configured with time rather than light intensity as the channel parameter. A similar technique was utilized to obtain the time profiles of luminescence under pulsed VUV (rather than gamma) excitation. These were performed at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY, which could generate repetitive high-intensity light pulses about 2 ns wide and 180 ns apart, monochromatized with a resolution of 0.25 nm, to wavelengths as short as 110 nm.

3. Results

The photo- and radio-luminescence spectra of YAP:Ce crystals have been extensively studied and published (see, e.g. [30, 31]). The spectra show the expected structure, with two close broad bands at about 350 and 375 nm characteristic of the d–f transitions of the Ce^{3+} ion. Except for some weak long-wavelength contribution [17], there is no appreciable emission other than that from cerium under any optical, γ- or x-ray irradiation.

3.1. Low-temperature thermoluminescence

In figure 1 we show the results of ltTL measurements on $YAlO_3$:Ce crystal in the range 15–300 K. Before each TL run the specimen was irradiated at 4 K with ultraviolet light of one of the following selected wavelengths: 300, 250, 237, 220, or 180 nm. We found

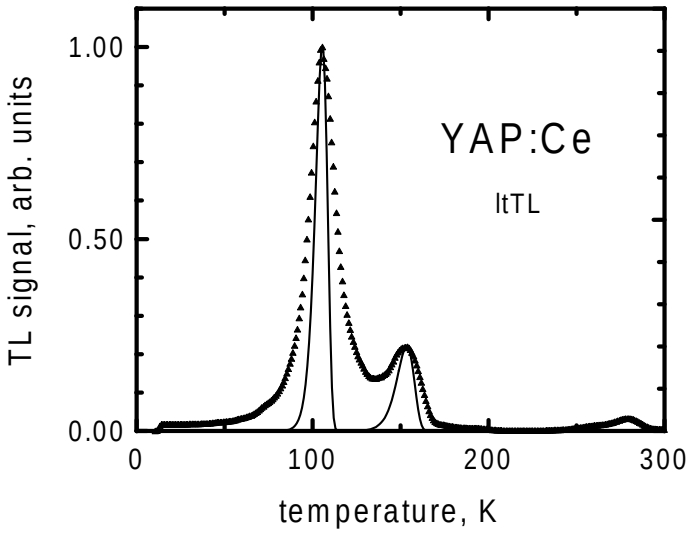

Figure 1. The thermoluminescence glow curve of YAP:Ce following VUV irradiation. Heating rate, 0.15 K s^{-1}. Full curves represent simulated glow curves calculated from a single-trap model. Trap parameters s and E for the major peak were chosen to provide the best fit to two different experiments; ltTL (this figure) and LY (figure 2).

that while the two longest of these produced only a very low TL signal, which was not much more than the background, irradiation at the shorter wavelengths (into higher Ce^{3+} f–d bands) gave progressively stronger TL signals, with the largest obtained from 180 nm irradiation. The progressive increase in TL signal with the energy of the excitation light can be readily understood in terms of the probability that this light will liberate an electron into the conduction band. While only the shortest of the selected excitation wavelengths has enough energy to cause photoionization directly, electrons raised into the upper d or s levels of the Ce^{3+} ion do have a small but finite probability of autoionization, which becomes greater the closer the upper level is to the conduction band. Any electrons that do reach the conduction band can, of course, migrate through the lattice, become trapped at a lattice defect and ultimately generate a recombination photon during the TL run. From the ratio of the total emission produced during the TL run to that produced by steady-state irradiation at 180 nm we estimated the probability of electron capture by a trap to be about 0.004, while for other wavelengths the value was much lower, probably reflecting the strong dependence of autoionization rate on electron energy.

The experimental points in figure 1 form a curve with two clearly resolved peaks, the most prominent at about 105 K and a satellite (with about 22% of the peak intensity) at 152 K. There is also evidence of other low-temperature contributions, which are barely detectable, at about 75 K and 280 K. While each of these individual features is presumably associated with its own unique type of trap, all the traps in each subset do not necessarily correspond to the same single discrete energy but, more likely, to statistical distributions around most probable mean values. Consequently, the calculations of glow curve shapes based on a simple model do not return unique values for the trap parameters. Instead, we find an entire family of (s, E) pairs that reproduce the positions of the two dominant glow peaks. This is because the rate of escape from traps is expressed in terms of the *product* of

the frequency factor s and the term $\exp(-E/kT)$, telling us nothing about the individual values. In order to select the right set, we must turn to other experimental measurements.

3.2. Scintillation light yield

The results of scintillation light yield measurements on YAP:Ce crystal in the range 90–400 K are shown in figure 2. The experimental points in the figure represent positions of the respective photopeaks, measured at a shaping time τ_{sh} of 0.5 μs. Since the closing of the time window (at about $2.35 \times \tau_{sh}$) discards any scintillation light that might be emitted after that, the resultant light yield value may change substantially depending on the decay time and relative amplitude of any delayed component. Thus when the scintillation light yield of a material that contains both radiative recombination centres (Ce^{3+} ions) and electron traps is measured against the temperature, the contribution coming from traps will vary because of the strong temperature dependence of the trap lifetime even when the steady-state light output, determined mostly by the Ce^{3+} ion quantum efficiency, stays constant [23]. The light yield (LY) against T curve will consequently assume a sigmoidal shape, as explained in detail by Wojtowicz *et al* [28]. Some aspects of the temperature dependence of LY have already been published [28], but subsequent improvements in the experimental set-up have now made possible more accurate measurements, particularly at the low end of the range. These reveal (see figure 2) an additional step-like feature in the LY against T curve between 100 and 120 K, indicating the existence of another, even shallower, trap.

It is the light yield results that enable us to choose the appropriate pair of (s, E) values from all those that fit the thermoluminescence traces. Since, like the TL, the relative amount of the scintillation light that is emitted more slowly than the radiative decay time of the Ce emitting centre is determined by the rate of escape from traps, it is similarly dependent

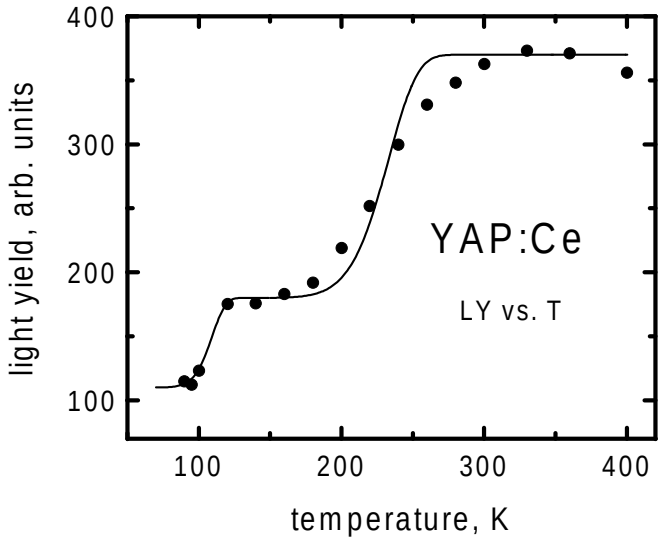

Figure 2. The scintillation light yield of YAP:Ce as a function of temperature. Experimental points, shown by circles, were obtained for 0.5 μs shaping time. The full curve represents the fit to experimental points from a two-trap model. Trap parameters s and E for a deeper trap were chosen to provide the best fit to two different experiments, ltTL (figure 1) and LY (this figure).

upon the product of s and $\exp(-E/kT)$. Consequently, when we plot $\log s$ against E, we find that all the values that satisfy the glow curve peaks fall on one straight line, while those that satisfy the light yield results fall on another having a different slope. Thus the intersection of the two lines establishes a correspondence between the step in the LY against T curve and the TL glow peak and identifies the only pair of (s, E) values that will satisfy both types of measurements. This is illustrated in figure 3, where the intersection of the lines designated 'LY' and 'ltTL' selects the one (s, E) pair appropriate to describe the effect of the primary trap (with the 105 K glow peak). This particular pair of values ($s = 7 \times 10^{11}$ s^{-1}, $E = 0.277$ eV) was used to calculate the full curve in figure 2. The fact that we can achieve a reasonably good fit to the experimental points in both the TL and LY measurements demonstrates their complementary nature, while the shallower slope of the experimental points relative to the calculated curve may be another consequence of our use of a single trap energy rather than a distribution, the same factor that contributes to the greater width of the experimental TL glow peak. It is also important to note that, despite the low temperature of the glow peak, the lifetime of the relevant trap at room temperature (293 K) turns out to be 82 ns, remaining even then slower than the radiative lifetime of the Ce ion. As we shall see, this has profound implications on the kinetic behaviour.

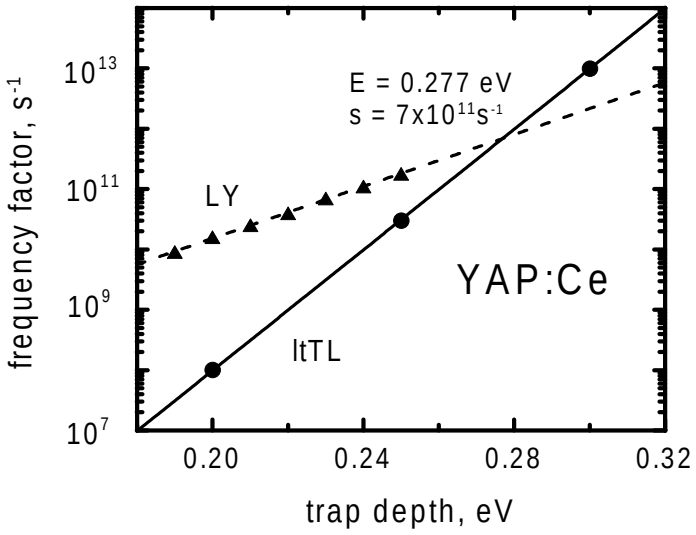

Figure 3. A diagram showing the relationship of the frequency factor s to the trap depth E. The full line, designated ltTL, is a straight line fit to points shown by circles, which correspond to pairs of ln (s) and E values obtained from the fit to the major thermoluminescence glow peak (figure 1). The dashed line, designated LY, is a straight line fit to points shown by triangles, which correspond to pairs of ln(s) and E values derived from the fit to the LY against T experiment (figure 2). The intersection of the two straight lines defines the best pair of s and E values to be assigned to the major shallow trap in YAP:Ce.

In principle, we could use a similar approach to analyse the effect of the two remaining traps, associated (respectively) with the glow peak at 152 K and the step-like increase of the LY at 100 K. Unfortunately, the effect on the light yield of the minor TL trap cannot readily be separated from that of the major trap. Consequently, we choose to assume the same frequency factor ($s = 7 \times 10^{11}$ s^{-1}), thereby deriving an energy depth from the location of its glow peak alone. This gives a value of 0.405 eV, and a room temperature

trap lifetime of 11.6 μs. As for the second LY-associated trap, the corresponding TL peak should fall at temperatures below 100 K, but no such feature can be clearly identified. Again assuming that this trap has the same frequency factor as the major trap ($s = 7 \times 10^{11}$ s^{-1}) we obtain from the LY fit alone an energy depth of 0.13 eV (figure 2, full curve). Since this trap has a room-temperature lifetime of only 240 ps, it may well be the 'ultrashallow' trap hypothesized by Wojtowicz *et al* in [28]. This trap is unlikely to exert any influence on the scintillation kinetics (light yield and scintillation time profiles) at room temperature beyond the earliest stages of the process and can therefore be safely omitted from further consideration.

The set of derived parameters for the two remaining traps that produce TL glow peaks includes not only frequency factors and energy depths, but also an approximate ratio of areas under those peaks (0.82:0.18). We must recognize, however, that the simulated glow curve, calculated using those parameters and shown by a full curve in figure 1, represents an approximation with only a single discrete energy for each trap, and could surely be improved with a more sophisticated description. However, it is not our purpose here to develop the best but the simplest model that can be most broadly applied to the various aspects of scintillation kinetics, and refinement will have to await future publication.

3.3. Kinetic measurements

Additional insight into the kinetic behaviour of the scintillation can be obtained from the decay traces of the Ce^{3+} emission. We have conducted a detailed study of optically and γ-excited luminescence time profiles of YAP:Ce at various temperatures. Some of these results, representative of general trends, are summarized in table 1. The decay times of the optically excited emission profiles of YAP:Ce at different temperatures have already been measured by other investigators [23], who find them to remain constant up to about 500 K. The parameters of single-exponential fits to all optically excited decays measured at one temperature (293 K) are summarized in table 1. Like the optically excited profiles, γ-excited profiles also show no measurable rise times, but, in contrast to them, their decays are no longer strictly single exponential. Their shapes are described quite faithfully by three exponential terms, with the dominant component at 16.7–26 ns. Only the initial fast component does behave in a relatively simple way, with a monotonic increase of amplitude

Table 1. Parameters derived from the fits to scintillation time profiles under optical and γ-excitation. Range refers to the upper time limit of the data points. The fitting parameters include: y_0, the baseline correction; A_1, A_2, A_3, the amplitudes; and τ_1, τ_2, τ_3, the decay time constants of the three single-exponential components.

Range	Excitation	T (K)	y_0	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)
110 ns	310 nm	293	20.7	3387	16.8	—	—	—	—
110 ns	245 nm	293	16.8	2357	16.8	—	—	—	—
110 ns	165 nm	293	30.55	2243	19.2	—	—	—	—
200 ns	Gamma	290	15.6×10^{-4}	0.955	25.72	0.033	179.3	—	—
200 ns	Gamma	200	132×10^{-4}	0.89	16.75	0.11	51	—	—
200 ns	Gamma	360	17×10^{-4}	1.05	21.5	—	—	—	—
5000 ns	Gamma	240	12.6×10^{-4}	0.913	17.47	0.07	131	0.019	615
5000 ns	Gamma	290	5.52×10^{-4}	0.977	25.8	0.038	137	0.0024	1115
5000 ns	Gamma	330	4.51×10^{-4}	1.017	22.7	0.01	180	—	—
5000 ns	Gamma	400	3.56×10^{-4}	1.024	20.26	—	—	—	—

with temperature (probably due to an increasing fraction of participating shorter-lived traps). At 290 K this component is clearly slower than at either higher (330, 360, and 400 K) or lower (240 and 200 K) temperatures. This is not, of course, a lengthening of the radiative lifetime but rather a direct consequence of the progressive decrease in trap lifetimes. At low temperatures, the traps are so long-lived that the only prompt component comes from Ce ions excited by unhindered carriers. At high temperatures, the lifetimes of most of the traps become shorter than that of the Ce ion, merely adding their own contribution to the Ce without introducing any delay. Around room temperature, however, the primary trap lifetime, while longer than that of the Ce emission, is too close to be separately resolvable, making for a longer initial component. The behaviour of the delayed components illustrates how consecutive fractions of deeper and deeper traps join and augment the fast component when the temperature increases.

A similar study has been recently reported by Tsushida *et al* [21] for YAP:Ce and other scintillator materials. In general, their results for YAP:Ce are consistent with ours, but with some differences that we attribute to a somewhat higher concentration of shallow traps in their samples. These include a higher contribution of longer components, as well as a slightly longer room temperature decay time of 32 ns. Unfortunately, the measured time profiles may vary so much from crystal to crystal as to limit the value of any systematic comparison.

In figure 4 we show the γ-excited decay of YAP:Ce at 293 K in the range 0–35 ns. The experimental trace is shown, along with a full curve calculated using the model to be discussed shortly. Note that at early times the decay is significantly slower than that shown by the dashed curve, which depicts the single-exponential 16.8 ns decay characteristic of the optically excited time profiles. Figure 5, with a logarithmic abscissa, shows that the delayed component persists to a microsecond time scale.

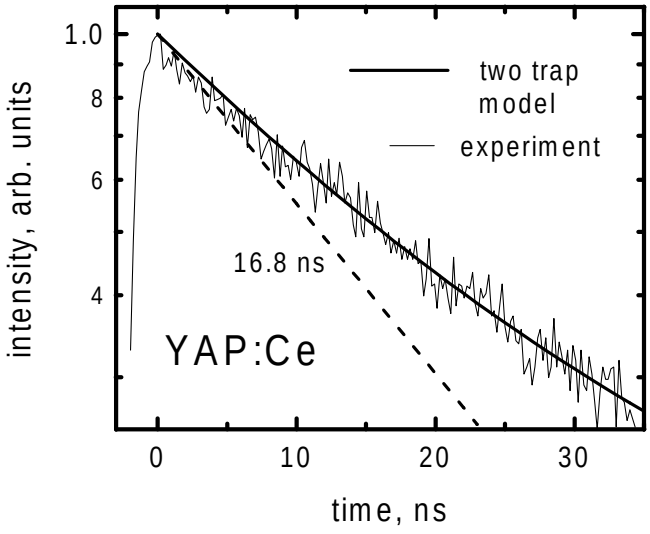

Figure 4. The scintillation time profile of YAP:Ce at 293 K, on a 35 ns time scale. The jagged line represents the experimental trace, while the full curve was calculated from the model (see text). The dashed curve shows a simulated decay corresponding to the radiative lifetime of Ce^{3+}.

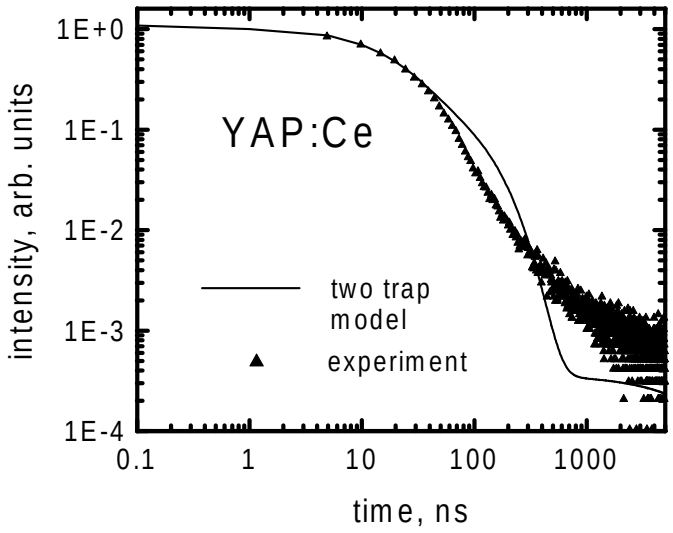

Figure 5. The scintillation time profile of YAP:Ce at 293 K, on a 5000 ns time scale. The experimental points are shown by small triangles, while the full curve represents a simulated decay calculated from the two-trap model, with no input from experimental decay measurements.

4. Discussion

4.1. The kinetic model

To develop a quantitative description of the scintillation process, we first assume that the material system consists of radiative recombination centres (Ce^{3+} ions) and electron traps, and is excited by a single high-energy ionizing particle that, essentially instantaneously, generates electrons in the conduction band and holes in the valence band. Next, we observe that free band hole lifetimes are usually extremely short, probably of the order of a few tens of picoseconds or less. Consequently, we would expect that all free valence band holes disappear almost immediately, distributed among the Ce^{3+} ions (generating Ce^{4+} entities) and other centres capable of capturing them. Since the latter will either produce extraneous emissions or relax non-radiatively (either of which constitutes a loss), we will term them *loss centres*. Although highly interesting, this stage of the scintillation kinetics is difficult if not impossible to access experimentally.

With the holes localized, the next chronological step in the evolution of the system is the decay of the non-equilibrium population of conduction band electrons, which proceeds on a time scale of some hundreds of picoseconds. Note that this phase of the scintillation process entirely determines the distribution of events that will ultimately take place: those electrons that were captured by Ce^{4+} ions (initial population $n^{3+*}_{Ce,0}$) will contribute to the *prompt component* of the scintillation; those captured by shallow and deep traps (initial population $n_0 \approx n^{4+}_{Ce,0}$) will contribute to the *slow components* in the scintillation time profile and to the *high-temperature thermoluminescence*, respectively; and finally, those captured by loss centres will not contribute at all, constituting an unrecoverable *loss*. If slow enough, this step can give rise to measurable scintillation rise times. We note, however, that very shallow traps can also contribute to an observable scintillation rise time, as has been suggested in the case of the LuAP:Ce [28].

As long as the recombination that sets up the original conditions takes a very short time of less than, say, 1 ns, as we have assumed it does, the initial concentrations are well defined, since both the Ce radiative lifetime and the trap lifetimes are much longer. Also, the presence or absence of loss centres has absolutely no influence on the evolution of the system beyond 1 ns. There is no need, therefore, to take them into account explicitly, since their net effect is merely to lower the efficiency of the host-to-ion energy transfer process [32] which is reflected in the lower initial concentrations of excited and ionized Ce ions and of electrons captured by traps.

Under these assumptions the entire process can be described by only a pair of equations [28]:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -np \tag{1a}$$

$$\frac{\mathrm{d}n_{Ce}^{3+*}}{\mathrm{d}t} = np - \frac{n_{Ce}^{3+*}}{\tau_{rad}} \tag{1b}$$

where n is the concentration of electrons in traps; n_{Ce}^{3+*} is the concentration of excited Ce ions; τ_{rad} is the excited Ce^{3+} radiative lifetime, and $p = s\exp(-E/kT)$ represents the thermally activated trap emission rate, where s and E are the frequency factor and trap depth, respectively. These equations can be applied to both the thermoluminescence [33] and scintillation kinetics [28], although with vastly different time scales and boundary conditions.

4.2. Thermoluminescence

In the TL process, the prompt emission, which decays completely after only a few hundred nanoseconds, plays no role whatever. With the pool of excited Ce^{3+} ions created by the initial recombination of conduction band electrons and Ce^{4+} ions long since depleted we get [33]:

$$I = \frac{n_{Ce}^{3+*}}{\tau_{rad}} = np = -\frac{\mathrm{d}n}{\mathrm{d}t}. \tag{2}$$

Consequently the intensity of the emission from the Ce^{3+} ions is determined exclusively by p, the rate of electron escape from their traps. Upon integration, assuming a linear heating rate $T = T_0 + \beta t$, we obtain the well known formula of Randall and Wilkins [34]:

$$I(T) = n_0 s \exp\left(-\frac{E}{kT}\right) \exp\left[-\left(\frac{s}{\beta}\right)\int_{T_0}^{T} \exp\left(-\frac{E}{kT}\right)\mathrm{d}T\right] \tag{3}$$

where $n = n_0$ and $T = T_0$ at the time $t = t_0$. The expression (3) that describes TL for first-order monomolecular kinetics was used to calculate simulated glow curves in figure 1. Note that the fitting parameters s and E were chosen to best reproduce both the glow peak positions (figure 1) and the temperature dependence of the light yield (figure 2). The values are a deliberate compromise, sacrificing a best fit for either of the two independent types of measurement in favour of simultaneously minimizing the errors associated with both. We could, of course, improve the fit (widening the calculated glow peak and decreasing the slope of the LY against T curve) by replacing the single discrete energy E with a distribution of such values, maintaining a common frequency factor. Unfortunately, this would introduce additional arbitrary parameters for which we have no direct measure. Nevertheless, even with our self-imposed constraints, the quality of the fit offers strong support for our approach and the model. Indeed, the application of equations (1*a*) and

(1*b*) in the frame of a simple discrete energy approximation gives even better fits to the high-temperature TL glow curve of YAP:Ce [26, 28], as well as both the htTL and ltTL curves of LuAP:Ce [28, 35], reproducing reasonably well both the locations and widths of the glow peaks, with consistent and physically reasonable values of the fitting parameters.

4.3. Scintillation kinetics and light yield

For scintillation kinetics, of course, the time scale is at the other extreme, since most of the scintillation light is emitted during the first hundred or so nanoseconds. Also, since the process is isothermal, the factor p must be a constant. Therefore, the solution of equations (1*a*) and (1*b*) can be expressed as [28]

$$n_{Ce}^{3+*} = n_{Ce,0}^{3+*} \exp\left(-\frac{t}{\tau_{rad}}\right) + n_0 \frac{p}{p-(1/\tau_{rad})}\left[\exp\left(-\frac{t}{\tau_{rad}}\right) - \exp(-pt)\right]. \tag{4}$$

In measurement of the scintillation light yield, the signal amplitude is proportional to the charge collected at the anode of the photomultiplier tube during a time window with a width of $2.35\tau_{sh}$. Consequently, the LY can be expressed as

$$\mathrm{LY} = \int_0^{2.35\tau_{sh}} I(t)\,\mathrm{d}t = \int_0^{2.35\tau_{sh}} \frac{n_{Ce}^{3+*}}{\tau_{rad}}\,\mathrm{d}t. \tag{5}$$

Substituting the value for n_{Ce}^{3+*} from equation (4) and integrating under the condition that τ_{sh} is significantly greater than τ_{rad}, gives

$$\mathrm{LY} \propto n_{Ce,0}^{3+*} + n_0 \frac{p\tau_{rad}}{p\tau_{rad}-1}\left[1 + \frac{1}{p\tau_{rad}}(\exp(-p\tau_{sh}) - 1)\right]. \tag{6}$$

This can be restated more conveniently by defining LY_0 as the sum of all electrons generated that went initially to Ce^{4+} ions or traps,

$$\mathrm{LY}_0 = n_{Ce,0}^{3+*} + n_0 \tag{7}$$

and expressing the branching coefficients a and b as the respective fractions of the total:

$$a = \frac{n_{Ce,0}^{3+*}}{n_{Ce,0}^{3+*} + n_0} \qquad b = \frac{n_0}{n_{Ce,0}^{3+*} + n_0}. \tag{8}$$

Applying these definitions, we obtain the final formula

$$\mathrm{LY} = \mathrm{LY}_0\left\{a + b\frac{p\tau_{rad}}{p\tau_{rad}-1}\left[1 + \frac{1}{p\tau_{rad}}(\exp(-2.35\tau_{sh}p) - 1)\right]\right\} \tag{9}$$

where a and b are the respective coefficients for the prompt direct and trap-mediated contributions, the trap emitting carriers at a rate p. Although equation (9) is expressed for only a single trap, expansion for additional ones is perfectly straightforward, since equations (1*a*) and (1*b*) are linear. Thus in the particular case of the two-trap model, we have two coefficients b_1 and b_2, for traps that emit carriers at two different rates, p_1 and p_2. We have also assumed, as discussed earlier, that the two traps share the same frequency factor, differing only in their energy depths, E_1 and E_2. The full curve in figure 2 was calculated from equation (9) for a shaping time $\tau_{sh} = 0.5$ μs and with values of $a = 0.3$, $b_1 = 0.19$, $b_2 = 0.51$, $E_1 = 0.13$ eV, $E_2 = 0.28$ eV, and $s = 7 \times 10^{11}$ s^{-1}. Here again we find good agreement between experimental data and the model, which predicts a two-step sigmoidal dependence of the light yield on temperature, with the steps at about 110 and 230 K. Again there are minor deviations, most likely due to our use of individual discrete trap energies rather than distributions, as discussed earlier.

The intensity/time profile in the case of two traps, one short-and one long-lived, is given by

$$I(t) = I_0\left[\frac{a}{\tau_{rad}}\exp\left(-\frac{t}{\tau_{rad}}\right) + \frac{b_1}{\tau_{sh}-\tau_{rad}}\left\{\exp\left(-\frac{t}{\tau_{sht}}\right) - \exp\left(-\frac{t}{\tau_{rad}}\right)\right\} + \frac{b_2}{\tau_{lg}-\tau_{rad}}\left\{\exp\left(-\frac{t}{\tau_{lg}}\right) - \exp\left(-\frac{t}{\tau_{rad}}\right)\right\}\right] \tag{10}$$

where τ_{sh} and τ_{lg} are the appropriate trap lifetimes and the parameters a, b_1, and b_2 are, as before, the fractions of the initial population of conduction band electrons that are captured by, respectively, Ce^{4+} ions, short-lived and long-lived traps. This formula has been used to calculate time profiles shown by full curves in figures 4 and 5. The coefficients were set at $a = 0.40$, $b_1 = 0.42$, $b_2 = 0.18$, and the decay times at $\tau_{sh} = 82$ ns and $\tau_{lg} = 11.6$ μs. (see table 2). These values, however, are not merely arbitrary parameters, derived from an empirical fit to the intensity/time experimental points. On the contrary, these parameters were derived without any input from the decay traces at all, but from the ltTL and LY calculations. Note that the agreement at either end is quite satisfactory, correctly predicting the slower than radiative initial scintillation decay (figure 4) and the occurrence of the slow component in YAP:Ce, as shown in figure 5. This component has previously been reported by other investigators [36]. The calculated curve does deviate somewhat from the experimental points toward the middle of the time range, but this deviation (as with the ltTL and LY fits) could well be correctable by giving adequate consideration to the energy spread within each type of trap. Moreover, while the commonly practised technique of empirical fitting as the sum of exponential terms would surely give better agreement, the resultant parameters would be merely descriptive, with little real physical significance. Our calculations, however, were made without using any data from the experimental decay measurements, and their physical significance is undeniable.

Table 2. Properties of shallow traps in YAP:Ce, as derived from TL and LY measurements. Traps are numbered according to the depth below the band edge. Energy values assume a frequency factor s of 7×10^{11} s^{-1}. The glow peak for trap 1 is inferred from LY only. The location of the LY step is defined by the point of inflection. The lifetime given for 'trap zero' is the Ce radiative value. The parenthesized LY values are renormalized to account for the absence of contribution from trap 3.

Trap	Energy (eV)	TL glow peak (K)	LY step (K)	Room-temperature lifetime (ns)	Room-temperature contribution to LY (%)
0	0			(16.8)	25 (31)
1	0.13	(51)	110	0.24	15 (18)
2	0.28	105	230	82	42 (51)
3	0.4	152		11 600	18

Note that the parameters in the light yield calculations are not the same as those in the scintillation decays. This is due to the fact that we are actually dealing with three traps, of which different pairs are relevant in the respective time scales. Thus, the 0.4 eV trap is easily visible from the glow peak at 152 K, and its contribution of about 22% of the major (105 K) peak must be reflected in the respective coefficients in the decay calculations. The 11.6 μs lifetime of this trap at room temperature, however, is too slow for its LY contribution to be recorded (most of it coming after the measurement window had closed), leaving its coefficient in those calculations as essentially zero. Similarly, the

0.13 eV trap is too shallow for its thermoluminescence to be recorded (its projected 50 K peak being too low for it to retain enough population during preirradiation to measure), but its influence can be felt in the small LY step at about 100 K. Since the 240 ps lifetime of this trap at 293 K is significantly shorter than the 16.8 ns radiative lifetime of Ce^{3+}, its presence is manifested in the room-temperature time profile of the scintillation as a 240 ps risetime [28]. Thus for the purposes of scintillation kinetics (figures 4 and 5) this contribution should be treated as an enhancement of the direct component, with the coefficients defined to reflect that. In the LY calculations (figure 2), of course, the contribution from this shallowest trap remains separately resolvable, and must be treated accordingly. The properties and effects associated with the various traps are summarized in table 2.

We find no evidence that deeper traps (0.4 eV or greater) make any contribution to the light yield at or above room temperatures, in agreement with the measurements of Korzhik *et al* [20]. This is not surprising, since the temperature would have to exceed 400 K for the lifetime of even a 0.4 eV trap to be reduced enough for its contribution to fit within the narrow scintillation measurement window. Even then, any such increase in LY could be more than offset by a thermally activated increase in the rate of trapping by htTL traps already identified in earlier work [26, 28], reversing the upward trend by allowing electrons to enter deeper traps whose barriers had previously made them inaccessible. We have omitted this possibility in the present treatment because the ltTL of YAP shows no evidence of such barriers. Such effects do appear to be present in LuAP [28], however, and have been included in the more rigorous development by Lempicki and Bartram [37], but the need to utilize numerical techniques makes the process considerably more complicated.

5. Summary and conclusions

The results of experimental and theoretical studies of recombination kinetics in the YAP:Ce scintillator material clearly demonstrate the interrelation of the low-temperature thermoluminescence, scintillation light yield, and scintillation time profiles. All these phenomena, including some unusual and heretofore unexplained properties of the YAP:Ce scintillator, can be interpreted in the framework of a simple kinetic model involving three relatively shallow traps, at about 0.13 eV, 0.28 eV, and 0.4 eV below the conduction band. The existence of two of these traps has been confirmed by the low-temperature thermoluminescence measurements, which reveal an inhomogeneously broadened double-peaked distribution. Despite the broadening, a simple discrete two-trap model accounts reasonably well for all of the experimental observations. We have established that a major trap, with a glow peak at 105 K, is responsible for the strong increase of the light yield between 200 and 300 K, and for the slower than radiative initial scintillation decay at room temperature. A secondary trap, glowing at 152 K, produces a much slower microsecond-scale component in the scintillation time profile. From measurements of the low-temperature thermoluminescence and the temperature dependence of the scintillation light yield, we find that at room temperature (293 K), only 25% of the electrons generated by the ionizing particle find their way directly to the Ce ion, with 15% passing through the 0.13 eV trap, 42% through the 0.28 eV trap, and 18% diverted into the 0.4 eV trap.

Using these values we can estimate the potential improvement in room-temperature performance that could be achieved in a hypothetical trap-free material. Such an estimate depends critically upon the shaping time used for measurement, since only those traps with substantially longer lifetimes could actually contribute to the loss. Thus with, say,

a 0.5 μs shaping time, only the minor trap glowing at 152 K could act as a source of loss, the other two being unable to retain electrons long enough to diminish the measured output. Consequently, given the branching ratios listed in table 2, the increase in light yield that could be achieved by the removal of the low-temperature traps would be only about 20%. However, for shorter shaping times (on the order of a few nanoseconds), significantly larger gains in the light yield would be expected, since the room-temperature lifetime of the 0.28 eV trap (glowing at 105 K) would then be long enough for it to act as a loss. Since the effective scintillation decay time at room temperature is 27 ns, this should roughly double the zero-time amplitude, assuming that all of the light is emitted in the single-exponential component of 16.8 ns. This would materially improve the timing resolution, making YAP:Ce, already characterized by exceptionally high -energy resolution, one of the best scintillator materials known today.

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