

## Kinetics of cerium emission in a YAG:Ce single crystal: the role of traps

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 1947

(<http://iopscience.iop.org/0953-8984/12/8/336>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.218

The article was downloaded on 15/05/2010 at 20:21

Please note that [terms and conditions apply](#).

## Kinetics of cerium emission in a YAG:Ce single crystal: the role of traps

E Zych<sup>†‡</sup>, C Brecher<sup>‡</sup> and J Glodo<sup>‡§</sup>

<sup>†</sup> Faculty of Chemistry, Wrocław University, 14 F Joliot-Curie Street, Wrocław, Poland

<sup>‡</sup> Chemistry Department, Boston University, 590 Commonwealth Avenue, Boston, MA 02215, USA

<sup>§</sup> Institute of Physics, N Copernicus University, Grudziadzka 5, 87-100 Torun, Poland

E-mail: zych@wchuwr.chem.uni.wroc.pl, cbrecher@chem.bu.edu and jglodo@phys.uni.torun.pl

Received 24 June 1999

**Abstract.** We have measured the emission spectra and decay kinetics of Ce-doped YAG under both optical and gamma excitation, at temperatures ranging from 60 to 600 K. The decay traces under gamma excitation display an unusual pattern of temperature dependence. Beginning with the lowest temperatures, the characteristic time constant of the decay coincides with the intrinsic (radiative) decay time up to about 180 K, at which point it suddenly jumps by more than 30%. The decay time remains longer than radiative until well above room temperature, then gradually reverts to the intrinsic value. This behaviour can be explained in terms of an array of shallow traps, whose existence is confirmed by the presence of thermoluminescent glow peaks. Depending on temperature, one or more of these traps acts as a temporary way-station for the free carriers that carry the excitation to the Ce ion, delaying its emission beyond what would be required by radiative decay alone.

### 1. Introduction

Although scintillator materials have been known for over a hundred years, only in the last decade have they been studied in any systematic manner. This recent surge of interest has been stimulated by the urgent and growing needs for improved radiological detectors in medicine, industry and high-energy physics. This research has yielded not only new scintillator materials of great promise [1, 2], but also significant advances in understanding the basic physics governing the scintillation process itself.

Basically, the practical potential of a candidate scintillator material is determined by how well it satisfies three major conditions:

- *High stopping power for the ionizing radiation.* This generally requires a host lattice with high density, a factor that becomes all the more critical the higher the energy of the radiation.
- *High efficiency of conversion of the energy of the stopped particle into visible radiation.* This requires not only the generation of the highest possible number of free charge carriers (electrons and holes), but their efficient migration to an emitting site and efficient recombination at that site to generate the detectable luminescence.
- *The kinetics of the resultant emission (rise and decay of the light pulse) must be much faster than the time scale of the process being measured.* This becomes increasingly important for higher radiation fluxes or for tomographic applications such as PET.

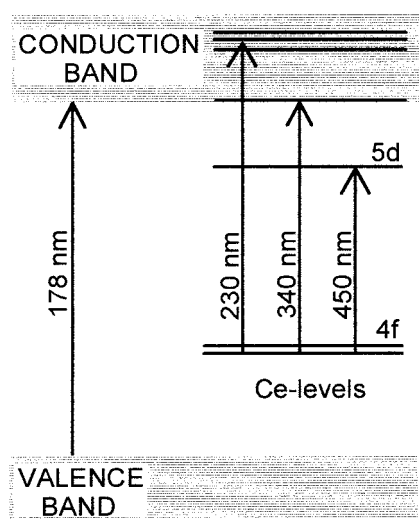
In practice, few materials excel in all three aspects. One that has received a great deal of attention in recent years is Ce-doped yttrium aluminium garnet,  $\text{Y}_3\text{Al}_5\text{O}_{12}$  or YAG [1]. It has a bright green emission peaking at about 525 nm, ideal for photomultiplier detection. It has a high light output of some 17 500 photons per MeV of ionizing radiation absorbed [3], more than twice that of bismuth germanate ( $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ , or BGO), the current standard. It has a decay time less than 100 ns, faster than most of the competing materials. And its density can readily be increased by some 50% by replacing the  $\text{Y}^{3+}$  cation with the heavier  $\text{Lu}^{3+}$ , with no significant effect on the emission [1, 4, 5].

The most intriguing aspect of the emission from Ce-doped garnets is their decay kinetics. Weber has measured the decay kinetics of YAG:Ce over a broad range of temperatures, 77–700 K, under direct optical excitation of the Ce ion [6]. His findings showed that up to some 600 K the decay can be expressed as a single exponential with a time constant of about 63–67 ns. Above 600 K the luminescence is rapidly quenched, virtually disappearing by about 630 K. Later measurements by Spowart *et al* [7] produced similar results. Under ionizing excitation, however [3, 4, 8, 9], the behaviour appears to be considerably more complex. One of the new features is the appearance of a rise time with a time constant of a few nanoseconds. This was discussed in detail by Moszynski *et al* [8, 9] who concluded that the rise time results from relatively slow overall transfer of energy from excited host to Ce. Another new feature observed only under ionizing excitation is a new *long* component having a time constant of a few hundred nanoseconds [3, 8, 9]. As was shown by Moszynski *et al* [9] the time constant of this component changes with Ce content, being shorter for higher concentrations. It has been clearly explained that the long component appears due to overlap between a Ce absorption band and a broad, slow excitonic emission peaking around 300 nm [9, 10]. This situation causes a delayed *radiative* transfer of energy to the Ce ion, which results in the appearance of a tail in the recorded decay. Thus the presence of both a rise time and a long component in the decay of Ce emission in YAG host were reasonably explained and are generally understood.

The behaviour of the *main* component of the Ce emission decay presents a far more difficult puzzle. At room temperature the time constant of this component under *ionizing* excitation runs in the neighbourhood of 85–87 ns, some 30% longer than under optical excitation directly into the Ce ion. Although repeatedly observed by other investigators, this interesting effect has received only perfunctory attention [3, 9]. Considering its obvious implications with regard to the processes of energy transport through the lattice, we felt that this effect warranted more detailed investigation. This paper presents some of the results of our effort.

## 2. Materials and experiments

The YAG:Ce single-crystal sample investigated in this work had dimensions of  $1 \times 1 \times 0.3 \text{ cm}^3$ , cut from a boule that had been pulled from the melt by means of the Czochralski technique by Litton Airtron. The specimen was optically polished before the measurements were done, and Ce content was measured analytically at about 0.5 mol%. The decay kinetics were measured using both optical and ionizing excitation, the former from a McPherson deuterium flash lamp, the latter with a  $^{137}\text{Cs}$  gamma source. The emission was monitored at the 525 nm luminescence peak of Ce with a McPherson 0.35 m monochromator. The spectrum of the emission was similarly recorded at various temperatures, along with the total light output. Thermoluminescence experiments were also performed, after irradiation at 4 K for 2 h with an  $^{241}\text{Am}$  x-ray source, followed by heating to 370 K at a rate of  $0.15 \text{ K s}^{-1}$  ( $9 \text{ K min}^{-1}$ ).



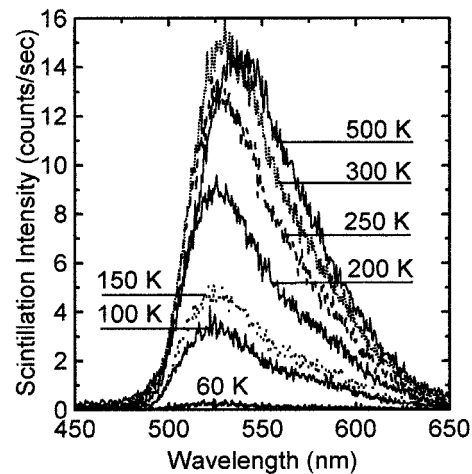
**Figure 1.** Schematic diagram of the energy level and band structure of YAG:Ce single crystal.

### 3. Results and discussion

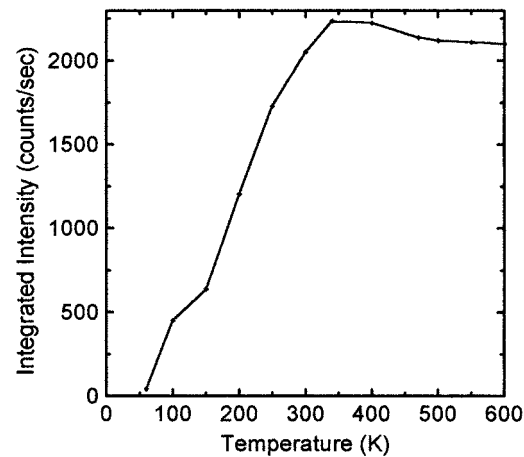
Figure 1 illustrates the structure of Ce ion energy levels together with the band structure of the host material as known from the literature [11, 12]. The primary excitation wavelengths are shown, with the absorbed energy ultimately feeding the emission from the lowest 5d level back down to the 4f terminal state, which is split into two components,  $^2F_{5/2}$  and  $^2F_{7/2}$ , by spin-orbit interaction. The spectroscopic measurements of this emission at the various temperatures are presented in figures 2 and 3, the former showing the spectra of the gamma-excited emission and the latter summarizing the temperature dependence of the total light emitted by cerium. From figure 2 we see little change in the shape of the emission as a function of temperature, except for a slight improvement in the separation of its two components upon cooling. The two constituents of the d-f emission arise because of the split 4f terminal level (see figure 1). As would be expected, the overall peak position shifts to the red roughly linearly with temperature, from 522 nm at 60 K to 538 nm at 550 K. Far greater changes, however, are seen in the overall intensity of the emission. Virtually undetectable below about 60 K, the emission becomes progressively more intense as the temperature is raised, reaching a maximum slightly above room temperature. It then becomes insensitive to further heating until the onset of thermal quenching at about 600 K, after which it rapidly drops off and disappears. A similar pattern has been found by Robbins *et al* for YAG:Ce (0.01%) under excitation by cathode rays [10].

While thermal quenching is obviously responsible for the lack of Ce emission above about 630 K, in agreement with Weber's kinetic data [6], the systematic intensity drop upon cooling below room temperature is more difficult to explain. The fact that the drop is not smooth and takes place over a wide range of temperature (more than 200 K) makes it even more puzzling. One might expect the free carriers (electrons and holes) created in the first phase of the scintillation event to become less mobile at lower temperatures, increasing the time needed for them to reach the Ce ion and raising the probability of nonradiative recombination. Such an explanation, while technically true in an overall sense, is far too simplistic to provide any insight into the actual mechanisms involved.

Now let us consider the decay kinetics. We begin with the two decay traces of Ce luminescence presented in figure 4. These decays were excited optically at room temperature



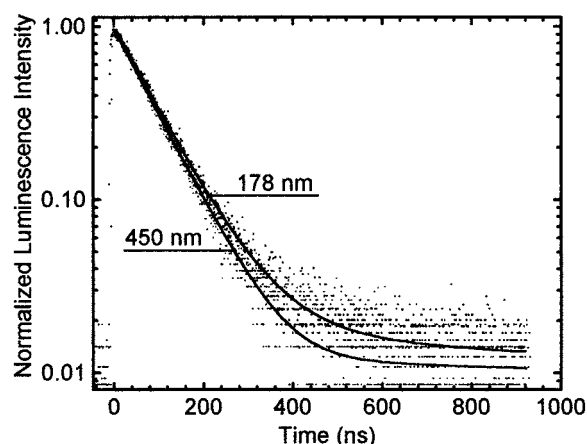
**Figure 2.** Emission spectrum of YAG:Ce single crystal under gamma excitation, at various temperatures.



**Figure 3.** Temperature dependence of total light yield emitted by YAG:Ce single crystal under gamma excitation.

at two different wavelengths: 450 nm, which promotes the 4f electron into the lowest 5d level of the  $\text{Ce}^{3+}$  ion; and 178 nm, which raises valence electrons all the way up to the conduction band (see figure 1). Since the energy gap in YAG is about 178 nm [11, 13, 14], optical radiation at this or shorter wavelengths can be considered ionizing radiation in the same sense as the more energetic gamma radiation, since they both cause ionization of the material. This further means that Ce emission caused by such excitation involves energy transfer from the host to Ce ion, as distinct from the longer wavelengths, which deliver excitation energy directly into the emitting Ce ion.

The differences in excitation wavelength have clearly observable consequences for the decay kinetics. The decay found for excitation by 450 nm light follows a single-exponential decay pattern with a time constant of 67 ns, in perfect accord with Weber's results [6]. The decay observed for ionizing optical excitation (178 nm), however, shows two major departures



**Figure 4.** Decay traces of YAG:Ce luminescence at room temperature, as a function of excitation wavelength.

from this pattern. One is that the decay requires at least two exponential terms, with a long component of about 320 ns clearly evident. On the basis of previous work [3, 8, 9] we can attribute this effect to the radiative transfer of energy from the longer-lived broad excitonic emission around 300 nm to Ce, which has an intense absorption in this region. Under 178 nm excitation, however, the time constant for the main component of the decay has increased to about 85 ns, almost 30% greater than the 67 ns found in the first case, but exactly what is reported for gamma excitation.

At this point we should interject a *caveat*. It is only when a decay can be described by a single exponential term that the fit can be imbued with unambiguous physical significance. Once a second or even a third term becomes necessary for an adequate mathematical description, it becomes just that—a *fit*—with no stronger connection to the real world than a polynomial or any other similar fit. Only the first term of a multiexponential fit retains any inherent claim to physical reality, and then (as is the case here) only when the primary term has a clearly dominant amplitude. It is only the *description* that is the sum of independent terms; the *process* rarely is.

Returning to the optically excited decays, we find that the same single-exponential pattern is maintained with only minimal variation in time constant for all wavelengths with energies substantially smaller than the band gap. These results at room temperature are summarized in table 1, which also includes parameters for gamma-excited decay. Comparison with figure 1 reveals that the three excitation wavelengths 450, 340 and 230 nm correspond to localized excitation of the Ce ion itself. Since these energies all raise a 4f electron to one of the 5d levels of the Ce ion we would expect the results to be the same, as indeed they essentially are. This is also effectively true of the 280 nm excitation, which, although initially absorbed by a lattice defect, migrates rapidly to the Ce ion, giving rise to the same behaviour [15]. However, when the excitation wavelength reaches 230 nm the time constant for single-exponential decay becomes definitely longer (73 ns) than at lower excitation energies, although still shorter than found under the delocalized excitation of 178 nm. We attribute this to a degree of delocalization of the Ce levels within the band structure of the host as presented in figure 1. Thus while 230 nm wavelength light does indeed raise the Ce 4f electron to one of its 5d levels, as is the case with 450 and 340 nm light, the level corresponding to the shorter wavelength lies well within the conduction band. Consequently there is a non-negligible probability for the

**Table 1.** Parameters describing shape of decay traces as sum of exponential terms.

Excitation wavelength (nm)	Decay time (ns)	Integrated magnitude (%)
450	67	100
340	68	100
280 <sup>a</sup>	66	100
230 <sup>b</sup>	73	100
178	85	96
	320	4
Gamma	88	71
	405	29

<sup>a</sup> Rapid nonradiative transfer into 340 nm Ce level from lattice defect state [15].

<sup>b</sup> The three highest 5d levels are too close to be excited separately.

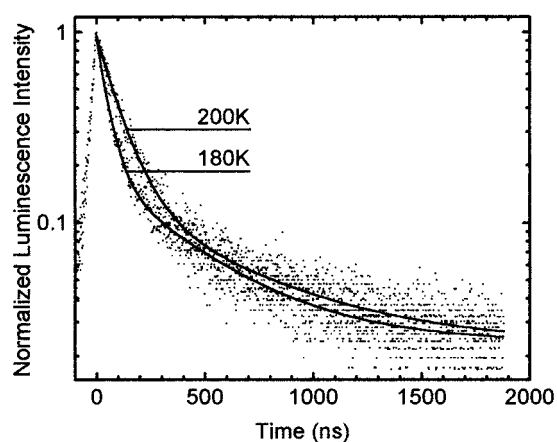
electron excited with 230 nm light to escape the Ce ion before relaxation, allowing it either to decay nonradiatively or to migrate to (and excite) another Ce ion. To the extent that the latter takes place, such excitation begins to take on some of the delocalized characteristics typical of ionizing radiation.

The partial delocalization of electrons excited by 230 nm light has been demonstrated by other investigators. Hamilton and Pedrini and co-workers [12, 16] performed a thorough research on photoconductivity in Ce-doped YAG, finding that only the lowest Ce 5d level is located well below the bottom of conduction band. The next one, absorbing at 340 nm, coincides with the very bottom of the band, giving rise to an extremely weak but definitely measurable photoconductivity signal. All the higher levels, of course, fall well inside the conduction band, allowing electrons excited to them with 230 nm light to escape the ion. This generates a strong photocurrent, a few orders of magnitude greater than obtained from 340 nm excitation. Having confirmed these results with our own photoconductive experiments [17], we must attribute the lengthening of the decay time for 230 nm to the escape of excited electrons to the conduction band, and their subsequent capture by another Ce ion.

The above hypothesis does not of course explain the mechanism by which the lengthening of the decay time actually takes place. To explore this question we performed a series of measurements of the decay kinetics over a broad range of temperatures between 60 and 550 K, utilizing gamma rays as an excitation source. At all temperatures the decay traces over a 500 ns window were reasonably well described as the sum of two exponential terms, a dominant one with a characteristic time ranging between 60 and 110 ns and a weaker one a factor of five longer. The amplitude of the slower term decreases significantly with rising temperature, in accord with the behaviour under cathode- and x-ray stimulation, reported by Robbins *et al* [10–20]. However, it is the behaviour of the shorter (dominant) component that is the most relevant for our purposes, and this is where we will focus our attention.

Closer examination of the early stages of the scintillation decay reveals a complex dependence upon temperature. As seen in figure 5, the shapes at various temperatures differ substantially from one another, and not even the first 250 ns of the decay can be adequately described by a single exponential term. The most striking differences can be seen between the 180 K and 200 K traces, with the higher-temperature decay being significantly slower at time zero but with much less curvature. Further heating to room temperature and then to 500 K brings a gradual increase in initial speed and a further reduction in curvature, which virtually disappears at the highest temperature.

Thus we must resort to a two-exponential fit for even the early stages of the decay. Since in the absence of competing nonradiative processes the decay time can never be shorter than the Ce<sup>3+</sup> intrinsic radiative value (and we see no contradictory evidence), we have arbitrarily selected this as the characteristic time for the first exponential term, removing it as a fitting



**Figure 5.** Decay traces of gamma-excited YAG:Ce emission at various temperatures. The differences in slope at time zero are readily evident.

**Table 2.** Parameters for two-exponential fit to first 250 ns of scintillation decay<sup>a</sup> of YAG:Ce.

Temperature (K)	Eff. decay. const. at time zero (ns)	Amplitude of radiative term (%)	Amplitude of delayed term (%)	Radiative decay constant (ns)	Time const. of delayed decay (ns)
130	73.1	86.5	13.5	63.8	958.6
150	64.2	89.9	10.1	64.2	$\infty^b$
170	64.5	88.6	11.4	64.5	$\infty^b$
190	85.1	70.5	29.5	64.9	334.4
200	106.9	40.9	59.1	65.1	190.0
210	99.4	47.5	52.5	65.3	184.9
230	89.9	57.8	42.2	65.7	181.9
250	87.8	60.8	39.2	66.1	176.9
270	86.0	61.8	38.2	66.5	163.5
295	90.2	51.1	48.9	67.1	139.7
320	82.3	60.5	39.5	67.6	122.7
330	77.3	76.0	24.0	67.9	137.4
350	75.1	85.4	14.6	68.4	150.7
370	74.6	85.7	14.3	68.9	177.1
400	73.3	93.1	6.9	69.7	213.0
430	73.1	94.4	5.6	70.5	251.0
470	72.5	98.9	1.1	71.7	$\infty^b$
500	73.8	98.4	1.6	72.6	$\infty^b$

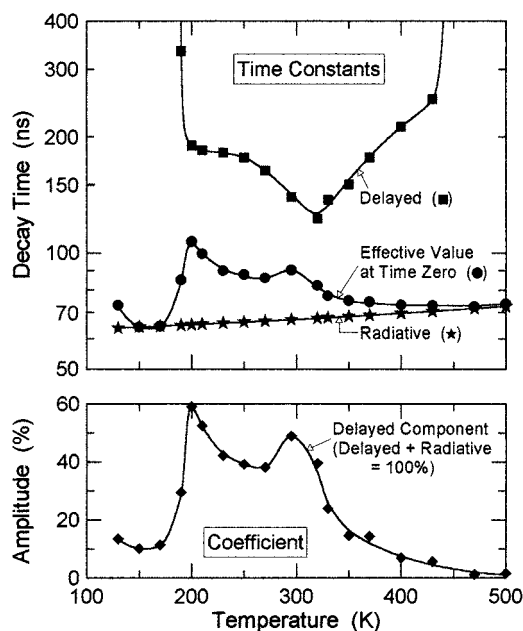
<sup>a</sup> Decays measured under irradiation from a <sup>137</sup>Cs source.

<sup>b</sup> Note:  $\infty$  denotes a quasi-DC component, with a time constant greater than 2  $\mu$ s.

parameter. The extent to which the decay departs from single-exponential behaviour is described by another exponential term with a longer time constant. The results of these fits are summarized in table 2.

We should emphasize that only the radiative decay time and the effective decay constant at time zero are physically measurable. The former, obtained by optical excitation, is nearly constant, with only a slight (and smooth) increase with temperature. In contrast, the latter, as seen in figure 6, is quite erratic, almost doubling over only a 30 K temperature increase, then taking another 200 K to wend its irregular way back down to the radiative value again. The other three items (two amplitudes and a time constant for the delayed component) are little more





**Figure 6.** Temperature dependence of parameters for two-exponential fit to decay of YAG:Ce emission. Note similarity between amplitude of delayed component and effective decay constant at time zero.

than *fitting parameters* and one should be cautious in attributing to them any direct physical significance. This is particularly true of the second time constant, which, as we shall see, really describes the cumulative effect from a number of different sources. Similarly, with experimental conditions unable to provide absolute intensities, the normalized coefficients can give only an idea of the relative magnitudes of direct and delayed excitation, offering no insight into the traps themselves. The temperature dependence of the various parameters are shown in figure 6.

But what is the mechanism responsible for these changes? Seeking an answer to this question, we turn to the phenomenon of thermoluminescence. This phenomenon has proven to be a powerful tool to investigate the presence of trapping centres in a material, including their depth and spatial abundance. Since it has already been demonstrated that traps can play a major role in the scintillation process in a variety of materials [21–23], it would be surprising if they did not also play a role here.

Let us examine how the process might take place. Just after an ionizing particle is stopped in the lattice, we find a  $\text{Ce}^{3+}$  ion immersed in a reservoir of free mobile electrons and holes. Excitation occurs when a pair of these free carriers recombine at the site of the ion. The most probable way for this to occur is through sequential capture by the  $\text{Ce}^{3+}$ , first of a hole to transform it to the 4+ state, then of an electron attracted by the net excess coulombic charge. Annihilation of the charge imbalance returns the Ce to the 3+ state but with sufficient excess energy that it must expel by emitting a characteristic photon. But anything that can provide competing sites where the carriers can be trapped is necessarily deleterious to the excitation process, either by providing alternative paths for nonradiative recombination or by trapping them for a long enough time to make them unavailable for useful emission. Either case must decrease the overall scintillation efficiency since some of the carriers are lost as potential excitation for the luminescent centre. And since lattice defects that can serve as trapping sites can be as abundant as Ce ions, their potential for mischief can be serious indeed.

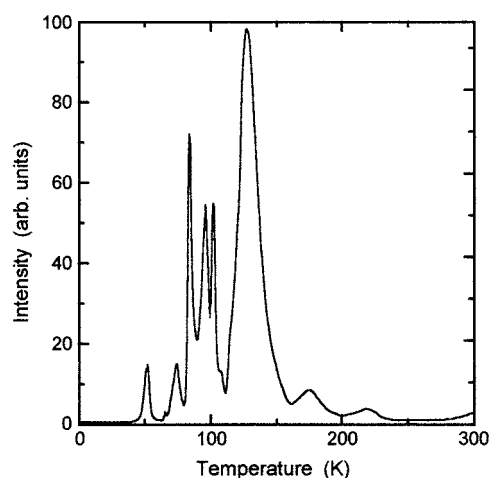


Figure 7. Thermoluminescence glow curve of YAG:Ce single crystal, after excitation by x-ray source.

Not all traps, however, are long-lived sinks for carriers. On the contrary, it has been shown [21] that many are rather shallow, allowing the trapped carriers to be thermally freed from them, making them *again* available for Ce. However, in such a case the excitation process would be *delayed* in time, since the trapping–detrapping route needs a finite time to take place. Since escape is thermally activated, the time a carrier spends in a trap is necessarily a function of temperature, following an Arrhenius type of relationship:

$$p = s \exp(-E/kT) \quad (1)$$

where  $p(= \tau^{-1})$  represents the rate of thermal ionization of the trap of depth  $E$  at temperature  $T$ , and  $s$  is a frequency factor, generally assumed to be independent of temperature. Thus the same trap may be deep enough to be a long-lived sink at one temperature, a short-term delay at a higher temperature and totally inconsequential at a yet higher one. And the temperatures at which thermoluminescent glow peaks occur can give us some insight into the spectrum of trap depths available in the lattice.

In figure 7 we show the glow curve recorded for the YAG:Ce single crystal under investigation. The thermoluminescence spectrum is quite complex, with at least eight well resolved peaks. At the lower temperatures (below 120 K) the peaks are quite sharp (5 K or less in width), along with two additional incompletely resolved shoulders. Above that temperature are three more peaks (including the most intense of the entire set), broader than the others by at least a factor of three, possibly indicating a different physical origin. These data are summarized in table 3.

It is important to note that the time scales of the two kinds of measurement, thermoluminescence and scintillation decay, differ by some nine orders of magnitude. But thanks to the Arrhenius relationship, a trap that requires 200 seconds to release its carriers at, say, 70 K (generating a TL glow peak) may hold them on average for only 200 ns at 200 K (merely delaying the Ce decay). Thus we attribute the sudden apparent lengthening of the decay time constant when the temperature exceeds 170 K to the thermally activated release of carriers from the shallowest trap, corresponding to the lowest glow peak. At this temperature the characteristic time constant for the relevant trap would be in the neighbourhood of 200 ns, which, when combined with the 67 ns contribution from directly excited Ce ions (which takes place at all temperatures), would simulate the behaviour of a single exponential in the 100 ns range. The Arrhenius relationship further dictates that the effect of any discrete trap energy can span only a limited temperature range, of the order of 20–30 K; beyond this the effective

**Table 3.** Characteristics of shallow traps in YAG:Ce.

Temperature of glow peak (K)	Trap depth corresponding to glow peak (eV)	Natural log of frequency factor	Temperature for trap lifetime of 150 ns (K)
52	0.129	26.2	137
74	0.185	26.2	204
83	0.242	26.2	238
96	0.258	26.2	279
102	0.274	26.2	297
(108)	0.292	26.2	316
(115)	0.324	26.2	335
127	0.364	30.0	295
(148)	0.447	30.0	363
175	0.506	30.0	411
220	0.634	30.0	515

Parentheses indicate poorly resolved peaks.

decay time must revert to the radiative value, because the trap lifetime on the low side is too long, and on the high side too short, to have much effect on the initial luminescence decay. But the glow curve shows major peaks at no fewer than eight different temperatures; this indicates the existence of at least that many different kinds of trap, each of which is characterized by a different and relatively narrow range of energy depths. We offer the hypothesis that the fortuitous spacing and distribution of these eight shallow traps are such as to assure the maintenance of an adequate population with a characteristic time constant in the critical 100–200 ns range from 200 K all the way up to and beyond room temperature.

Let us test whether the proposed model gives a reasonable simulation of the observed behaviour. Assuming first-order monomolecular kinetics (not always valid, but close enough in the early stages of decay), and a linear heating rate  $T = T_0 + \beta t$ , the shape of the thermoluminescence glow curve for each trap can be described by the well known formula of Randall and Wilkins [24]:

$$I(T) = n_0 s \exp \left[ (-E/kT) - (s/\beta) \int_{T_0}^T \exp(-E/kT) dT \right]. \quad (2)$$

This contains two unknown parameters, the trap depth  $E$  and the frequency factor  $s$ . As discussed by Wojtowicz *et al* [22, 23], the glow peak determines uniquely only the *product* of the frequency factor with the energy exponential (i.e. the rate of escape from the trap at any given temperature), and not the individual values. These must be identified on the basis of other criteria; Wojtowicz, working with the orthoaluminates of yttrium and lutetium, was able to use the temperature dependence of the scintillation light output. But this requires a small number of well resolved glow peaks and equally well resolved jumps in the light yield, conditions which YAG does not meet. We do, however, have a different set of data at our disposal, namely the decay traces at many different temperatures. While most of these traces show the effects of more than one trap, there is one place where a single trap may be separately quantifiable: the point at which the initial decay time shows its sudden jump. As indicated in table 2, the characteristic time of the slower component changes by a factor of 1.76 in only a 10 K interval, at a temperature where no other traps can influence the decay. This is the critical point: if indeed no other traps contribute at these temperatures, as both the sharp jump in decay time and the spacing of the lowest two glow peaks seem to indicate, then the second exponential term of the fit would truly have a direct physical significance, giving us the characteristic time for this trap at *two* temperatures. With this information, we can then solve equation (1) uniquely for both the trap depth and the frequency factor, obtaining a value

of 0.185 eV for the trap depth  $E$  and 26.2 for  $\ln s$ , an ideal fit to the glow peak at 74 K. Then, applying the same frequency factor to all of the other sharp glow peaks (below 120 K), we can derive the corresponding trap depths, as listed in table 3. The reason for assigning a different frequency factor for traps above 120 K will be seen shortly.

With these quantities in hand, it takes little effort to calculate the effect of these traps upon the decay kinetics. As asserted earlier, each trap introduces a 20–25 K window during which its characteristic time falls within the critical 100–200 ns range where its effect on the decay is most readily observed. With each window overlapping its neighbours, the overall decay time is maintained substantially longer than the intrinsic Ce radiative value over a range of 150 K. Meanwhile, as the characteristic time of the previous trap drops below the radiative lifetime of the Ce ion, its influence on the decay vanishes, causing the amplitude of that component to increase accordingly. As the temperature rises, the cumulative increase in the prompt excitation available for the radiative component reduces the relative influence of the next deeper traps, leading to a gradual downward trend of the overall decay time (see figure 6). The relevant temperatures at which each trap exerts its maximum influence are also given in table 3.

Note that only the glow peaks between 70 and 110 K are needed to account for the entire delayed decay phenomenon. The one peak below them (52 K), corresponding to the shallowest trap, serves only to explain the slight upturn in decay time at the lowest temperature of measurement (130 K). It is sufficiently well separated from the others to allow the decay time to drop back to the intrinsic Ce radiative value between 150 and 170 K, before the effect of the others can be felt. Similarly, the two highest temperature glow peaks correspond to traps too deep (and probably too sparse) to contribute any significant effect. This leaves only the peak at 127 K, whose trap depth, if we use the same frequency factor as for the lower temperature peaks, would assert its influence above 350 K, just where we actually see the decay settling back to its radiative value. If, however, we assume a greater frequency factor ( $\ln s \approx 30.0$ ), its decay contribution will move down to room temperature, where it might be responsible for the upward bump around that temperature (see figure 6). Consequently, we choose to calculate the trap depth for this glow peak, as well as those at yet higher temperatures, using the greater value for the frequency factor.

The presence of traps has consequences for many aspects of the scintillation process. Although we have focused on their effect upon the primary decay component, the influence of traps is felt in the shape of the entire decay pulse, to the limits of detectable signal. The inexorable lowering of the trap time constants as the temperature rises will be felt in the slow component as well, signalled by a waxing and waning of its amplitude and time constant. This effect, however, cannot be separated from the independent contribution attributed to a transfer from the excitonic emission discussed earlier, which would dominate the thermal behaviour of the emission tail.

We also note that the integrated intensity of the total gamma-excited emission does not exhibit the same temperature dependence as the decay traces. While the time constant of the primary decay component is greatest at around 200 K, the intensity does not reach its maximum value until significantly above room temperature, where the decay constant has essentially returned to the radiative value. This is fully consistent with the trap model, since it is only when all thermal detrapping of carriers is faster than the radiative lifetime that they all become available to excite the emitting centres.

#### 4. Summary and conclusions

We can summarize our findings as follows: We attribute the unusual kinetic behaviour of Ce-doped YAG to the presence in the lattice of an unusual abundance of as many as 11 shallow

traps. At the lowest temperatures these traps act in the traditional manner as long-lived sinks, diverting a fraction of the free electrons and holes that carry the excitation and withholding them from the emitting Ce centre. As the temperature rises, however, the time during which the traps can immobilize the carriers becomes progressively shorter, to the point where the rate of escape from the shallowest set approaches the radiative decay rate. This acts as a secondary reservoir to provide a delayed feed of excitation to the Ce, lengthening the effective decay time. As the temperature rises further, the succeeding traps, one by one, come into play, extending the effect to above room temperature. Finally, when the temperature is high enough to lower all the trap lifetimes below the radiative decay time, the measured decay reverts to its original value. With the traps no longer functioning, the total intensity of the emission now reaches its maximum value. Thus the model is consistent with all our experimental observations.

### Acknowledgments

The authors express their appreciation to Professor A Lempicki for his assistance and encouragement during the course of this investigation. We also gratefully acknowledge the support provided by the US Department of Health and Human Services, Public Health Service (NIH), under grant R01 CA62330-04, and by the Polish Committee for Scientific Research (KBN), under grant 3 T09B 031 16, in various aspects of this work.

### References

- [1] See e.g. Lempicki A, Wojtowicz A J and Brecher C 1996 *Wide-Gap Luminescent Materials: Theory and Applications* ed S R Rotman (Norwell, MA: Kluwer)
- [2] Blasse G and Grabmeier B C 1994 *Luminescent Materials* (Berlin: Springer)
- [3] Zych E, Brecher C, Wojtowicz A J and Lingertat H 1997 *J. Lumin.* **75** 193
- [4] Trendler R C (ed) 1995 *Conference Record, 1994 IEEE Nuclear Science Symp. Medical Imaging Conf.* (Piscataway, NJ: IEEE) p 307
- [5] Lempicki A, Randles M H, Wisniewski D, Balcerzyk M, Brecher C and Wojtowicz A J 1995 *IEEE Trans. Nucl. Sci.* **42** 280
- [6] Weber M J 1973 *Solid State Commun.* **12** 741
- [7] Spowart A R and Fairley E J 1978 *Nucl. Instrum. Meas.* **150** 159  
Spowart A R 1979 *J. Phys. C: Solid State Phys.* **12** 3369
- [8] Moszynski M, Ludziejewski T, Wolski D, Klamra W and Norlin N O 1994 *Nucl. Instrum. Methods A* **345** 461
- [9] Ludziejewski T, Moszynski M, Kapusta M, Wolski D, Klamra W and Moszynska K 1997 *Nucl. Instrum. Methods A* **398** 287
- [10] Robbins D J, Cockayne B, Glasper J L and Lent B 1979 *J. Electrochem. Soc.* **126** 1213
- [11] Tomiki T, Akamine H, Gishiken M, Kinjoh Y, Miyazato M, Miyazato T, Toyokawa N, Hiraoka M, Hirata N, Ganaha Y and Fudemma T 1991 *J. Phys. Soc. Japan* **60** 2437
- [12] Hamilton D S, Gayen S K, Pogatshnik G J, Ghen R D and Miniscalco W J 1989 *Phys. Rev. B* **39** 8807
- [13] Mürk V and Yaroshevich N 1994 *Phys. Status Solidi b* **181** K37
- [14] Mürk V and Yaroshevich N 1995 *J. Phys.: Condens. Matter* **7** 5857
- [15] Wong C M, Rotman S R and Warde C 1984 *Appl. Phys. Lett.* **44** 1038
- [16] Pedrini C, Rogemond F and McClure D S 1986 *J. Appl. Phys.* **59** 1196
- [17] Levy B *et al* to be published
- [18] Robbins D J, Cockayne B, Lent B and Glasper J L 1979 *J. Electrochem. Soc.* **126** 1556
- [19] Robbins D J, Cockayne B, Lent B, Duckworth C N and Glasper J L 1979 *Phys. Rev. B* **19** 1254
- [20] Robbins D J, Cockayne B, Glasper J L and Lent B 1979 *J. Electrochem. Soc.* **126** 1221
- [21] Lempicki A and Bartram R H 1998 *J. Lumin.* **81** 13
- [22] Wojtowicz A J, Glodo J, Lempicki A and Brecher C 1998 *J. Phys.: Condens. Matter* **10** 8401
- [23] Wojtowicz A J, Glodo J, Drozdowski W and Przegietka K R 1998 *J. Lumin.* **79** 275
- [24] Randall J T and Wilkins M H F 1945 *Proc. R. Soc. A* **184** 366